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Laboratory Evaluation of Remediation Alternatives for U.S. Coast Guard Small Arms Firing Ranges

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16. Abstract (MAXIMUM 200 WORDS)

The purpose of this study was to identify and investigate technologies that may be effective in reducing soil contamination resulting from current or past U.S. Coast Guard (USCG) small arms firing range (SAFR) activities. The study identified USCG SAFRs and selected those that were either representative of typical USCG activities or were sites with a high probability that corrective measures would be needed in the near future. After the ranges were identified, soil samples were collected and evaluated to determine the effectiveness of physical and chemical treatment processes in removing metal contaminants from the soil. Both physical separation and extraction technologies appear to have merit when applied to the USCG soils. Physical separation and chemical extraction were not effective for all the soils, but each technology was effective for at least one of the soils tested. Electrokinetic remediation technology appears to be effective for all soils. Regardless of the technology applied, all the alternatives will produce a metal-contaminated residual that will require disposal or additional treatment. The volume of this residual produced will depend on the technology applied and the amount of contamination in the soil.

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Executive Summary

One of the primary missions of the United States Coast Guard (USCG) is the enforcement of laws and treaties. To implement this responsibility, many USCG members must be trained in the use of small arms (pistols and rifles). As a result of small arms training, firing ranges have become contaminated with concentrations of lead, copper, and antimony. These metals are toxic, with lead being the primary metal of concern due to its higher concentration. Once the range is no longer used for its intended function, it can be classified as a waste site and be subject to remediation under the Resource Conservation and Recovery Act.

The USCG requested that the U.S. Army Corps of Engineers Waterways Experiment Station research the feasibility of using various technologies to treat soil that has become contaminated as a result of USCG small arms firing range (SAFR) activities. This research included site selection, sample collection, soil characteristics analysis, and laboratory-scale treatment technology evaluation.

The study identified USCG SAFRs and selected those that were either representative of typical USCG activities or were sites with a high probability that some form of corrective measures would be needed in the near future. The four sites chosen for study were the : Training Center in Cape May, New Jersey; Integrated Support Command (ISC), Ketchikan, Alaska; ISC, Kodiak, Alaska; and the Communications Station in New Orleans, Louisiana. After these ranges were identified, soil samples were collected and evaluated in the laboratory to determine the effectiveness of physical and chemical treatment processes in removing metal contaminants from the soil.

The laboratory analyses included identification of soil characteristics such as soil type, metals content, and particle size distribution. These characteristics provide an indication of which remediation technologies are likely to be effective on that particular soil. Soil remediation technologies were the primary focus of the laboratory investigations. These technologies are designed to reduce contaminated soil mass. This is accomplished by either producing a small, highly concentrated contaminated residual and a clean large volume soil mass, or through the removal of the soil's contaminants in their entirety.

The technologies tested on the USCG soils included physical separation, chemical extraction, and electrokinetics. Both physical separation and extraction technologies appeared to have some merit when applied to the USCG soils. Physical separation and chemical extraction were not effective for all four soils, but each technology was effective for at least one of the soils tested. Only the electrokinetic remediation technology appears to be effective for all four soils. Regardless of the technology applied, all the alternatives will produce a metal contaminated residual that will require disposal or additional treatment. The volume of this residual produced will depend on the technology applied and the amount of contamination in the soil.

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Introduction

One of the primary missions of the United States Coast Guard (USCG) is the enforcement of laws and treaties. To implement this responsibility, many USCG members must be trained in the use of small arms (pistols and rifles). As a result of small arms training, firing ranges have become contaminated with concentrations of lead, copper, and antimony. These metals are toxic, with lead being the primary metal of concern due to its higher concentration. The USCG Office of Environmental Management is responsible for identifying and remediating contamination at USCG facilities. They asked the Research and Development (R&D) Center to assist in the investigation of USCG small arms firing ranges.

In May 1996, the R&D Center contacted the U.S. Army Corps of Engineers Waterways Experiment Station (WES) to obtain information about ongoing research being conducted at WES in the heavy metal contaminated soils area. As a result this inquiry, the USCG requested that WES initiate research to evaluate the feasibility of using various treatment technologies to treat soil which has become contaminated as a result of USCG small arms firing range (SAFR) activities. The WES initiated this research effort in August of 1996, and this report presents the finding of this effort.

Objective of Report

The purpose of this report is to present the findings of laboratory investigations that evaluated the applicability of physical separation and chemical extraction technologies for treating contaminated soils at selected USCG SAFRs. The focus of this study was to identify and select SAFRs that were either representative of typical USCG activities or had a high probability that some form of corrective measures would be needed in the near future. After these ranges were identified, soil samples were collected and evaluated to determine the effectiveness of physical and chemical treatment processes in removing metal contaminants from the soil. Several physical treatment processes were evaluated in this study. They included soil particle size separation by sieving, wet shaker tabling, and attrition scrubbing. Chemical treatment processes evaluated were batch extraction tests, pilot extraction studies, and electrokinetic (EK) studies.

Report Organization

This report is presented in four main parts:

1. Introduction - The introduction provides a summary of what a SAFR is and the types of ranges. The background of metal toxicity and how metals migrate- from a SAFR are also introduced along with the regulations that may affect SAFRs. Next, a summary discussion is presented of why and how the four USCG sites were selected for evaluation. The locations of the four sites are presented along with a short site history and a description of the soil properties. This is followed by a brief overview of potential SAFR remediation technologies.

2. Materials and Methods - This section discusses the methods for the sample collection and laboratory tests associated with this study. Details of the bulk and core soil sampling, processing, and characterization are provided. An extensive array of potential treatment technologies are identified and discussed.

3. Results - Results of all the testing methods are discussed in this section.

4. Conclusion and Recommendation - This section provides conclusions and brief recommendations based on the results of the tests.

Background

Small Arms Firing Ranges

The term small arms firing range (SAFR) typically includes a vast array of ranges. This report will only address the outdoor pistol and rifle training ranges used by the USCG. A typical SAFR consists of a firing position (the point of weapon firing), a cleared down range area, a target position, and an impact berm, as shown in Figure 1.
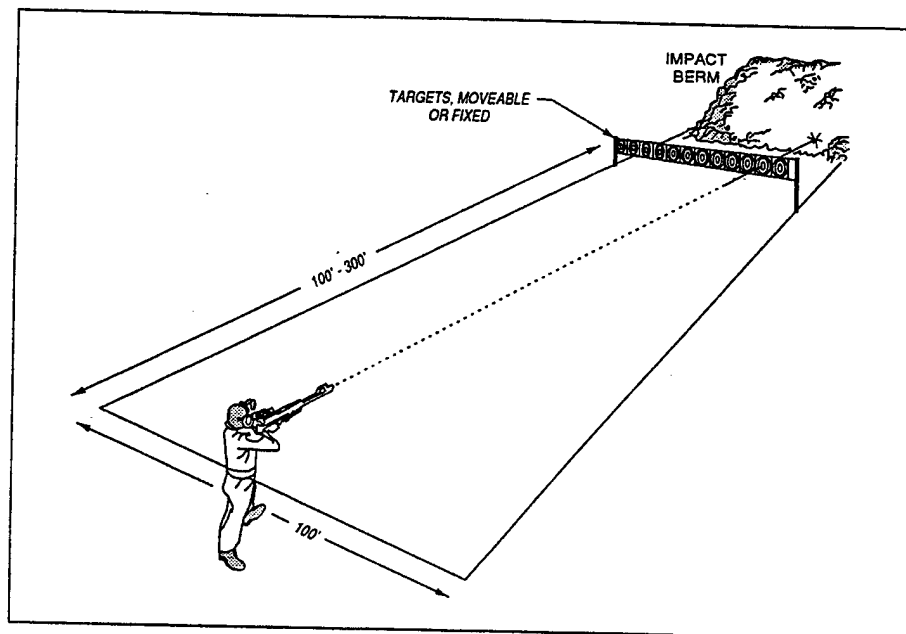
Figure 1. Typical small arms firing range.

The Army has a variety of SAFR, but generally groups these ranges into three classes: zeroing ranges, familiarization ranges, and qualification ranges. Most USCG SAFRs are configured like the 25-meter zeroing range shown in figure 2. At most military ranges the shooter is stationary, however, at USCG activities the shooter may move and fire at different distances; thus the firing line position may vary. Typical USCG weapons consist of 9-mm pistol rounds, M16-5.56 mm machine gun rounds, and shot gun OO-buck rounds. Historically, 45-cal. pistol and M1 carbine

rounds have also been extensively used. Normal training may involve the use of one or all of these weapons.
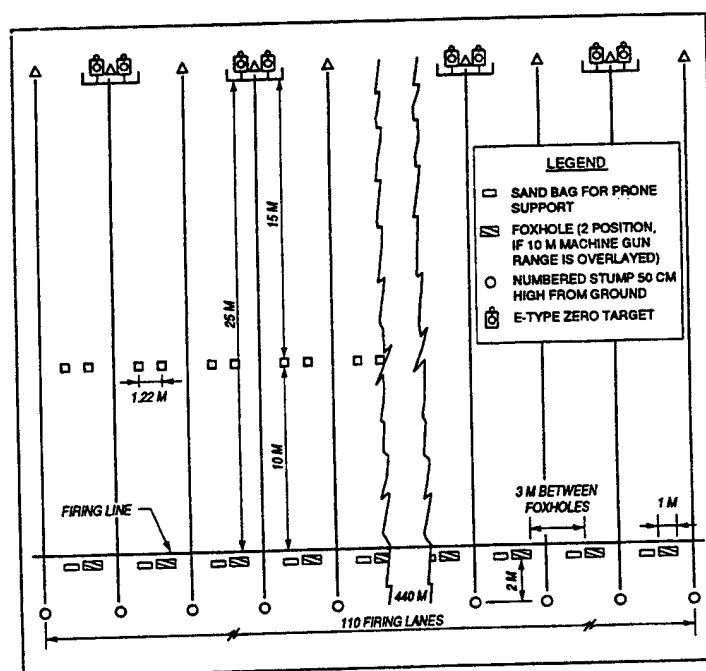
Figure 2. A 25-m (82-ft) zeroing range.

Environmental Issues at SAFRs

The main environmental concern associated with SAFRs involves spent munitions. Typically, projectiles (bullets) are fired at a target and, after passing through the target, are stopped in a berm or the soil located behind the targets. After years of use, the bullets from the small arms activities build up in the soil. The projectile rounds utilized at SAFRs typically consist of a copper-jacketed bullet and a lead core. As shown in Table 1 and Figure 3, the bullets are primarily composed of lead and copper. As illustrated in Table 1, lead accounts for up to 67percent of the weight of the projectile and therefore constitutes the greatest environmental concern.

Table 1. Typical metal composition of 5.56 mm projectiles.

Ball Type	Weapon	Metal Concentration in Percent			
		Antimony(Sb)	Copper (Cu)	Iron (Fe)	Lead (Pb)
5.56 mm	M16	0.4	31.3	-----	67.3
5.56 mm (Hardened Tip)	M16	1.0	35.4	12.7	50.9

The quantity of lead (Pb) and copper (Cu) that may accumulate in a SAFR berm can be extensive. Using conservative estimates of training, it is estimated that over 14,000 pounds of lead will accumulate in the berm of a single SAFR on an annual basis.

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PROJECTILES

5.56 MM

JACKET

LEAD SLUG

STEEL TIP

LEAD SLUG, 32 GR
= 52 % OF BULLET

7.62 MM

LEAD SLUG

COPPER
JACKET

LEAD SLUG, 114.5 GR
= 77 % OF BULLET

0.50 CALIBER

COPPER
JACKET

LEAD SLUG

STEEL SLUG

LEAD FILLER, 11.5 GR
= 1 % OF BULLET
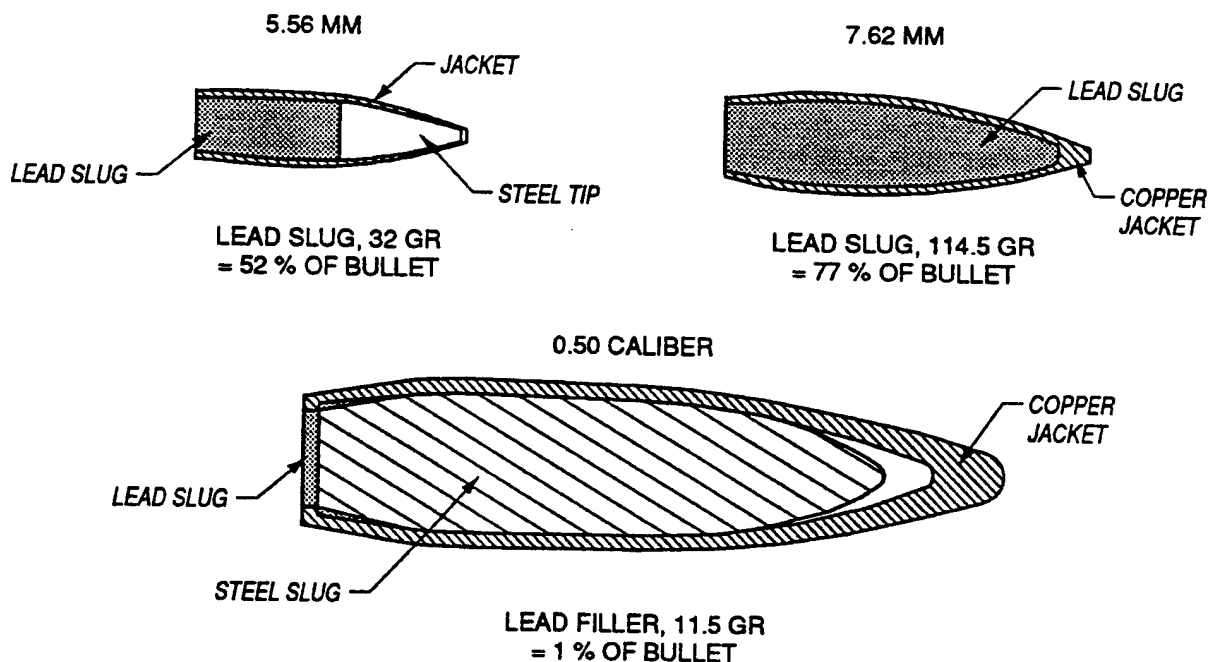
Figure 3. Drawing showing cross-sections of bullets.

Summary of Metal Toxicity

The Safe Drinking Water Act (SDWA) passed by Congress sets the primary drinking water standard to 50 g/l of lead. Even at levels below the drinking water standard, serious brain, kidney, and nervous system damage has been documented (Gale et al., 1994). Lead blood levels of >0.05 mg/kg or urine levels >0.08 mg/kg are associated with lead poisoning.

Copper, in contrast, has little or no human toxicity. However, copper is known to effect small organisms and has been used as a fungicide in many industrial and agricultural applications. The maximum contaminate level in drinking water for copper is 1 part per million (ppm).

Antimony is a silvery or gray shiny metal or yellow crystal. It is used to make metal alloys, enamels, rubber compounds, and matches. Antimony is considered a hazardous substance and is regulated by the Occupational Safety and Health Administration (OSHA). Repeated exposure may cause danger to the liver and heart muscle. However, antimony has not been tested for its ability to cause cancer in animals.

Zinc is not known to be a carcinogen. OSHA does not regulate it, and no target organs have been identified. Contact with skin or eyes may cause severe irritation or burns. Prolonged exposure may cause dermatitis.

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Metals Migration at SAFRs

Metals have two primary mechanisms for migrating from a SAFR. They can be transported from the range horizontally, resulting in surface-water contamination. They can also migrate vertically, potentially impacting the groundwater.

Horizontal Transport

Horizontal migration generally occurs during heavy rain, where the metals are transported through quick moving surface runoff to nearby streams. Metal particles transported through this type of migration generally produce localized contamination due to the density of metals. As the velocity of the transporting water slows, the metals drop from solution and are deposited on the surface. Horizontal metal migration also occurs via sediment transport. Metals tend to attach to the fine material in the soil. Lab tests (Bricka 1996a) indicate that in many instances metals concentrate in the fine fraction of the soils (less than 63 μm). Small soil particles heavily contaminated with metals are easily transported in the suspended and dissolved solid fraction of the water. Suspended matter containing metal contamination may settle far from the range, resulting in substantial accumulation of metal in the sediment of local streams near SAFRs.

Vertical Transport

Metals also have the potential to migrate from SAFRs to groundwater via vertical transport. This occurs because the metals are in constant contact with the soil pore water, which can become saturated with dissolved metals. The infiltration of rainwater can flush the pore water and carry contamination to the groundwater. However, the capillary action of the soil and evapotranspiration may mitigate contaminant migration. After the contaminant enters the groundwater, subsurface horizontal transport in the groundwater will be the predominant transport mechanism disseminating the contaminants from the source.

Many factors influence the rate of vertical transport of the metal contaminants, including soil chemistry, water chemistry, metal speciation, atmospheric precipitation, site topography, wetting and drying cycle, freezing and thawing cycles, groundwater depth and velocity, and bullet type. Once the metal is dissolved, factors such as the soil organic content, metal oxides, metal carbonates and metal sulfides, soil clay content, and soil cation exchange capacity can affect metal solution chemistry. Each factor contributes to the retention or release of the metals by the soils. Vertical transport of metal contaminants is a complicated process involving many soil and pore water interactions.

Theory of Metal Migration

For metals to migrate vertically from a SAFR, two things must occur: first, the metals must be dissolved in the pore water; and secondly, these dissolved metals must migrate via bulk transport. Bulk transport involves the movement of the contaminants from the pore water into the groundwater flowing vertically and horizontally. Soil chemistry, water chemistry, metal speciation, and projectile type will be the main variables affecting metal dissolution. The bulk

transport will be influenced by atmospheric precipitation, site topography, wetting and drying cycles, and depth to groundwater.

Factors Affecting Pore Water Concentration

While SAFRs projectiles primarily contain lead, copper, and antimony, lead is by far the most toxic and is the greatest environmental concern. Thus, this discussion will focus primarily on lead contamination. One major factor affecting pore water concentration is the compound in which the lead is found (speciation). Metal speciation is influenced by hydrogen-ion concentration (pH) and redox potential (Eh) within the soil. Many metals species of lead consist of salt complexes. Most common salts of lead are relatively insoluble or only slightly soluble with the notable exceptions of lead nitrate and lead acetate (table 2). (A high solubility constant (Ksp) indicates high solubility.)

Table 2. Solubilities of some common salts of lead.

Compound	Symbol	Ksp	Sol (g/cc)	Color
Lead acetate	$Pb(C_2H_3O_2)$	10.1	------	white
Lead carbonate	$PbCO_2$	$3.3x10^{-14}$	0.00011	white
Lead chloride	$PbCl_2$	$1.6x10^{-5}$	0.99	white
Lead chromate	$PbCrO_4$	$1.8x10^{-14}$	$5.8x10^{-6}$	orange
Lead fluoride	PbF_2	$3.7x10^{-8}$	------	white
Lead hydroxide	$Pb(OH)_2$	$1.42x10^{-20}$	0.0155	white
Lead nitrate	$Pb(NO_3)$	5.88	56.0	white
Lead orthophosphate	$Pb(PO_4)_2$	$3x10^{-44}$	$1.4x10^{-5}$	white
Lead di-orthosilicate	$Pb_2Si_2O_7$	Insol.	------	white
Lead oxide	PbO	$1.2x10^{-15}$	0.0017	yellow-red
Lead di-oxide	PbO_2	Insol.	------	black, dark brown
Triplumbicterte oxide	Pb_3O_4	Insol.	------	red
Lead sulfate	$PbSO_4$	$1.6x10^{-8}$	0.00425	white
Lead sulfide	PbS	$8x10^{-28}$	0.006	black

Source: Peters et al. (1976)

Lead generally occurs in three oxidation states: elemental lead having a valence of (0), divalent lead (+2), and tetravalent lead (+4). At natural water pH (3-9) and Eh [0.6-(-0.6)], divalent lead is the predominant valence. Soil chemistry can also affect lead concentrations. Materials such as complex-forming ligands and chelating agents may increase or decrease the solubility of lead. The effects of dissolved organic matter (represented by fulvic acid) serves to increase the solubility of lead in the pH range of 4 to 6. Figure 4 illustrates how fulvic acid and lead species affect the solubility of lead in groundwater.
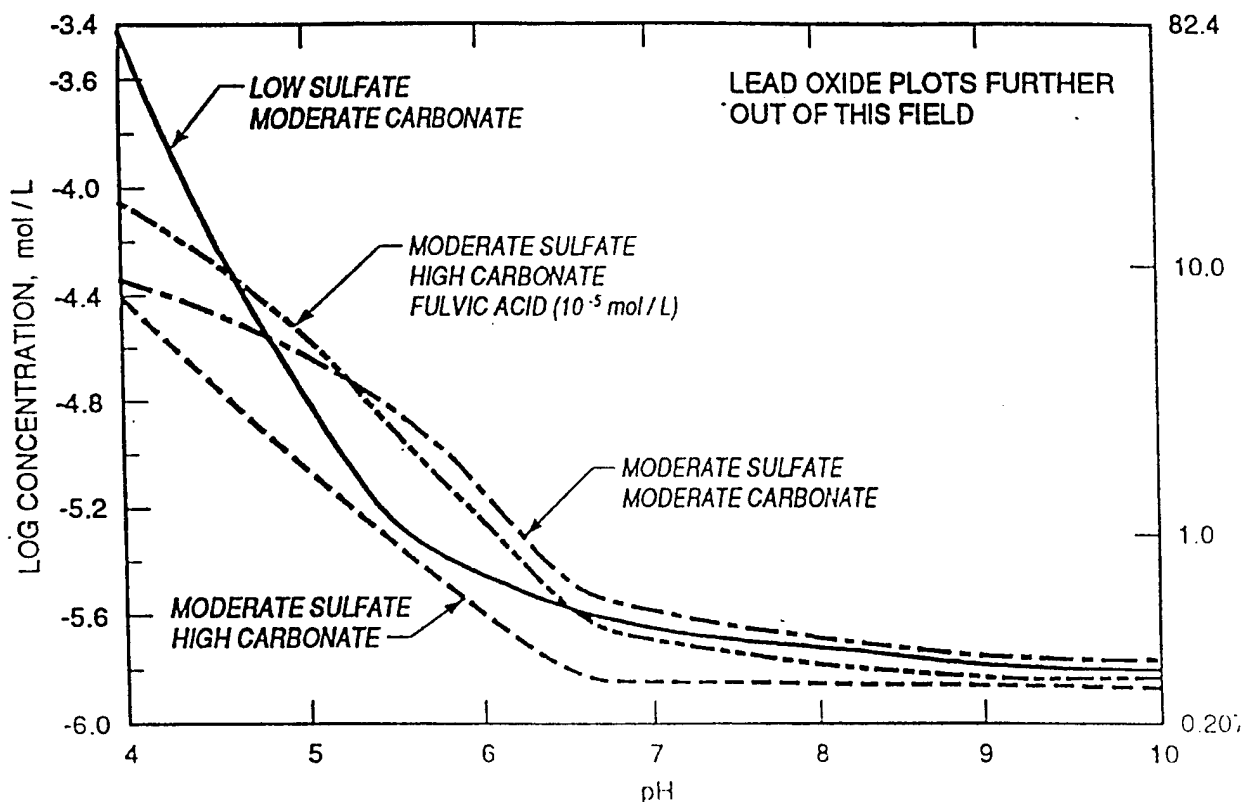
Figure 4. The solubility of lead in three different groundwaters (Source: Heath et al., 1991).

Soil organic matter and clays that are insoluble can affect exchange capacity (typically contribute to the clay or organic soil fraction) and also significantly influence pore water lead solubility. The decay of soil organic matter, such as pine litter, may also produce organic acids. These acids will lower soil pH and increase the solubility of lead. Ionic concentration, influenced by soil chemistry, may also have significant effects on lead solubility (Allen, 1993).

The type of bullet will also have a significant effect on pore water lead concentration. Generally there are two theories on how the lead is transported from projectiles to the pore water. Johnson et al. (1993) reports that as the bullets enter the soil, "the lead is molten and soft and sticks to the silicate grains of the soil, thus smearing on the soil surface." The lead in the soil is solubilized from the soil's surface to the pore water. The other theory involves galvanic corrosion effects. Most military projectiles are copper-jacketed and, as the projectile enters the soil, the jacket is fractured. The copper in the jacket either remains in contact with the lead core or is separated.

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Regardless if separation occurs or not, lead (Pb) and copper (Cu) build-up in the soil occurs at the SAFR after extended periods of use. When the metals become wetted through a rain event, an electrical connection between two dissimilar metals is established, and an electron flow occurs between the metals resulting in galvanic corrosion. With galvanic corrosion, dissolution of the least resistant metal is increased, and dissolution of the more resistant metal is decreased (Fontana, 1978). As illustrated in Table 3, Cu has a higher electromotive force (EMF) (+0.337) than Pb (-0.126) and thus is nobler, forcing the dissolution of Pb into the pore water.

Table 3. Standard EMF series of metals.

	Metal-Metal Ion Equilibrium Unit Activity	Electrode Potential Versus Normal Hydrogen Electrode at 25°C, volts
	Au-Au^{+3}	+1.498
	Pt-Pt^{+2}	+1.20
	Pd-Pd^{+2}	+0.987
	Ag-Ag^{+}	+0.799
	Hg-Hg^{+2}	+0.788
	Cu-Cu^{+2}	+0.337
Noble or Cathodic		
	H$_2$-H^{+}	0.000
Active or Anodic		
	Pb-Pb^{+2}	-0.126
	Sn-Sn^{+2}	-0.136
	Ni-Ni^{+2}	-0.250
	Co-Co^{+2}	-0.277
	Cd-Cd^{+2}	-0.403
	Fe-Fe^{+2}	-0.440
	Cr-Cr^{+3}	-0.744
	Zn-Zn^{+2}	-0.763
	Al-Al^{+3}	-1.662
	Mg-Mg^{+2}	-2.363
	Na-Na^{+}	-2.714
	K-K^{+}	-2.925
Source: Fontana and Greene (1978)		

Little information regarding the corrosion potential for bullet projectiles at SAFRs was available when this theory was first considered. To investigate this theory, a study was initiated in the summer of 1995 by WES to examine the galvanic corrosion effects of the bullets. Preliminary results for this study were released in an internal report (Bricka, 1996b). Results of this study indicate that, as theorized, galvanic corrosion is a major factor contributing to the lead pore water concentration.

Factors Affecting Bulk Transport

Rainfall, as well as site topography, greatly influences the bulk transport of lead. Water must flow through the vadose zone to the aquifer for groundwater contamination to occur. If there is little or no precipitation, there will be no vertical bulk transport of the contaminants. If precipitation is excessive and this water travels through the vadose zone, contaminants in the pore water will be diluted by the water flow. Site topography affects bulk transport by increasing or decreasing water infiltration to the vadose zone. If the site is significantly sloping, most of the surface-water will run off and little infiltration will occur. In contrast, if the site is relatively flat, more infiltration will occur.

Wetting and drying cycles of the soil will also affect bulk transport. As the soil dries, an increase in the concentration of the lead in the pore water will occur, increasing metal precipitation and sorption. If the soil becomes completely dry, the lead will be in a solid form resulting in a change in the metal species. As the soil is re-wetted, additional species transformation will occur which may increase (or decrease) the bulk transport of the lead.

Regulations Addressing SAFR

This section is provided as a brief introduction to the regulations that may effect SAFRs. It is not intended to be a complete list of all regulations but simply to provide limited background on SAFR regulations.

Munitions rule

On August 12, 1997, the Final Rule 40 CFR Parts 260 et al. (USEPA, 1997) for military munitions hazardous waste identification became effective. This rule addresses the larger arena of weapons impact training areas which includes large weapons such as bombs and missiles but also blankets SAFRs. This rule establishes the regulatory definition of solid waste as it applies to three specific categories of military munitions: 1) unused munitions, 2) munitions being used for their intended purpose, and 3) used or fired munitions. Under this ruling, unused munitions are considered to be a solid waste for regulatory purposes when: 1) the unused munitions are abandoned by being disposed of, burned or incinerated, or treated prior to disposal; 2) the unused munitions are removed from storage for purposes of disposal or treatment prior to disposal; 3) the unused munitions are deteriorated, leaking, or damaged to the point that they can no longer be returned to serviceable condition and cannot be reasonably recycled or used for other purposes (except recycling by "discard" [i.e., placement on the ground], unless such placement is the result of use as a munitions, or burning for energy recovery); or 4) the munitions have been determined by an authorized military official to be a solid waste.

Range Rule Overview

A separate ruling is currently being compiled by the Department of Defense (DOD), referred to as the Range Rule (USEPA, 1999). The proposed Range Rule is a five-phase process that addresses closed, transferred, and transferring military ranges. While this rule has not been promulgated, it currently indicates that projectiles from a SAFR are not considered as waste material until that range is no longer used. If the soil from a berm is not classified as a waste, it is not regulated under the Resource Conservation and Recovery Act (RCRA); thus it cannot be a hazardous waste. Once the range (or berm) is no longer used for its intended function, it can be classified as a waste site and be subjected to RCRA. One must be aware that currently the range rule is only recommended policy. Each state agency may interpret the munitions rule differently as it applies to SAFR activities in their area of jurisdiction.

Clean-up Standards for Lead Contaminated Soil

A uniform standard for when action should be taken to remediate metal (lead) contamination or to what level the metal must be removed to declare that soil "clean" does not currently exist. These "action level" or "clean up standards" vary from state to state and from site to site. They also depend on final land usage after remediation. Some state agencies will consider a soil clean if the soil passes the criteria for Toxicity Characteristic as defined by the U.S. Environmental Protection Agency (USEPA, 1992). If a soil has lead concentrations less than 100 mg/kg, it will pass the Toxicity Characteristic (Bricka, 1996a and 1996b), thus soils with greater than 100 mg/kg lead become a concern.

The state of Minnesota, for example, has a cleanup standard of 100 mg/kg for residential property and 1200 mg/kg for industrial land use (USAEC, 1997). In July 1994, the EPA announced an action level of 400 mg/kg for bare residential soil (Moshman, 1997). Clarification over different lead regulations is being considered by the USEPA. In June 1998, USEPA officials proposed a rule under section 401 of the Toxic Substances Control Act (TSCA) to identify lead-based paint hazards. These include hazardous lead paint as well as residential dusts and soils that have levels of lead considered to be hazards (regardless of whether they were contaminated with paint or other lead sources). That document sets a "soil-lead hazard" at 2,000 ppm and included recommendations to remediate hazardous soils that meet or exceed that level, such as soil removal or capping. USEPA Superfund officials protested because the draft rule appeared to contradict cleanup guidance issued by the Superfund program, which identifies soil "screening" levels at 400 ppm. The proposed 2,000 ppm hazard level for lead in soils is not a final level and may change in response to public comments (USEPA, 1998).

In summary, lead clean-up criteria is a moving target. Each site (or SAFR) clean-up criteria should be negotiated with the environmental regulatory agency within each state prior to initiating any remediation. For this study, only the propensity of a specific remediation technique for removing the soil contaminants is presented. The ability of a remediation technique to meet specific clean-up criteria must be evaluated on a case by case basis.

Sites of Interest

Site Selection Methodology

One of the first tasks in this effort was to determine the USCG SAFR sites that should be visited for sample collection. An in-depth effort was initiated to identify the USCG facilities that are currently utilized or have had SAFR activities. Ten USCG SAFRs were identified as a result of that effort. These ranges were ranked in order of priority, considering the following factors:

- the throughput of projectiles (more bullets result in a larger lead source);
- the age of the range (older ranges have more lead and more weathered bullets);
- the type of weapons used at the range (jacketed weapons pose more long-term problems than unjacketed weapons);
- whether or not the range is still active (an active range may not be subject to RCRA);
- whether there is a berm that is no longer utilized (an unused berm is probably subject to RCRA);
- whether there's contaminated soil stored on site (would be regulated by RCRA and could be in violation of 90-day storage requirement);
- whether the facility is experiencing OSHA problems at the range; and
- soil type (could affect vertical migration).

Table 4 presents the rank prioritization of that investigation, the top priorities being the SAFRs at (a) New Orleans, Louisiana, (b) Ketchikan, Alaska, (c) Honolulu, Hawaii, and (d) Petaluma, California to be considered for sampling.

The scope of work for this study allowed for two sites to be sampled and studied. Although not required, four sites were actually sampled and included in this effort. These sites were:

- USCG Training Center Cape May, NJ
- USCG Communications Station New Orleans, LA
- USCG Integrated Support Command Kodiak, AK
- USCG Integrated Support Command Ketchikan, AK

Communication Station New Orleans and Integrated Support Command (ISC) Ketchikan ranges were selected because they were the top two sites on the prioritized list. Training Center Cape May was included because it is the most used SAFR within the USCG. The SAFR at ISC Kodiak was also sampled since consideration was being given to reconfigure the range and place a bullet trap at this range. This information would have moved these sites up in the ranking but was not available until after the report supporting table 4 was completed.

Integrated Support Command Ketchikan

ISC Ketchikan supports USCG activities in Alaska. ISC Ketchikan is located on Revillagigedo Island and is one mile south of downtown Ketchikan, figure 5. ISC Ketchikan is host to five tenant units: two cutters; Station Ketchikan, a small boat station with two 41-foot utility boats; Electronics Support Detachment Ketchikan, a detached unit of Electronic Support Unit

Table 4. Range description and ranking.

WES RANK	SITE	RANGE TYPE	MUNITIONS USED	BERM	BULLET TRAP	RANGE USAGE	SOIL TYPE
1	New Orleans, Louisiana	Outdoor, 27 yards	9 mm, M-16, and 12 gauge shotgun	Berm excavated and placed on site in 1995	None	M	Inceptisols
2	Old Range Ketchikan, Alaska	Outdoor 25 yards	9 mm, M-16, up to 50 caliber, and 12 gauge shotguns	Natural hill side	None	M	Spodosol
3	Sand Island, Hawaii	Semi enclosed	9 mm, M-16, and 12 gauge shotgun	Earthen collection system, soil in front of bullet trap with lead contamination	Metal, 45 degree	H	Mollisols
4 (tie)	Petaluma, California	Outdoor, 50 yards	9 mm, M-16, and 12 gauge shotgun	Bullet trap installed in front of old berm	Metal	H	Alfisols
4 (tie)	Training Center, Cape May, New Jersey	Semi-enclosed	9 mm, M-16, and 12 gauge shotgun	Bullet trap installed in front of old berm	Metal	H	Utisols
5	Kodiak, Alaska	Outdoor, 25 yards	9 mm, M-16, and 12 gauge shotgun	Natural hillside	None	M	Inceptisols
6	Galveston, Texas	Outdoor 25 yards	9 mm, M-16, 22 caliber, and 12 gauge shotgun	Berm constructed of Ocean material	None	L	Vertisols
7 (tie)	Portsmouth, Virginia	Semi enclosed	9mm, 10 mm, M-16, 12 gauge shot gun; 45, 7.72, 38 and 40 caliber handguns	Berm excavated, disposed of and replaced by contractor in 1996	Wooden baffles overhead and on sides	H	Ultisols
7 (tie)	Reserve Tracen Yorktown, Virginia	Indoor/outdoor	9 mm, M-16, and 12 gauge shotgun	Berm excavated, disposed of and replaced by contractor in 1995	Metal	M	Ultisols
8	New Range Ketchikan, Alaska	Semi enclosed	9 mm, M-16, up to 50 caliber, 12 gauge shotguns	None	Rubber mats staked vertically	M	Spodosol

Ketchikan; and an Armory Detachment. Personnel stationed at ISC Ketchikan must undergo training with various small arms as part of their overall mission. An onsite SAFR is located at Ketchikan for this purpose.
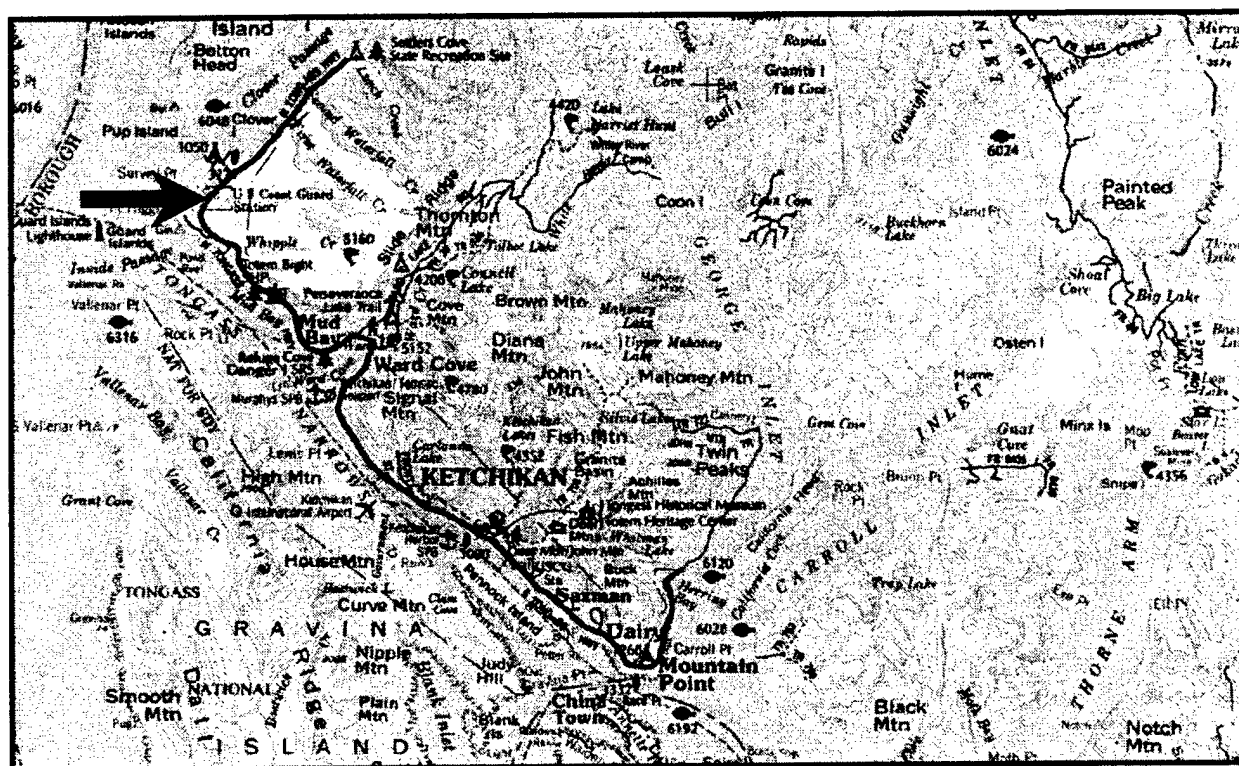
Figure 5. Location of ISC Ketchikan on Revillagigedo Island.

A new semi-indoor range has been constructed at Ketchikan for personnel firearms qualifications. This new SAFR is a four sided, exposed ceiling, cement floored facility. The bullet trap consists of a lamellate rubber collection system. Also at the Ketchikan site is an outdoor firing range which has been deactivated. Soil samples were collected only from the area around the deactivated outdoor SAFR.

The outdoor range is approximately 300 feet long and 30-40 feet wide and has six firing positions or lanes. The actual date of construction for the outdoor range could not be determined, but the USCG discontinued use of this range in 1995 when the new semi-indoor range was completed. The range appears to have been in operation for 30 to 40 years.

A perimeter walk of the site indicated that there was a small wooden structure at the southwest end of the site, which served as a cover for the range firing positions. Wood decking covered the area from the firing position to the target area (approximately 75 ft). A wooden walkway also exists on the left side of the range and is approximately 25 ft in length. It appeared as though a wooden walkway at one time existed, which circled behind the new firing range to the west side of the new semi-indoor range parking area. The range was constructed into a natural hillside, which served as an impact berm. This hillside was approximately 250 ft from the firing line.

Investigation into past range usage revealed that, in addition to use as a typical 25 meter range, approximately 110 feet downrange targets were positioned in a tire pile and at various points in front of this area. Site personnel explained that 50 caliber and M-16 weapons had been used at this site, as well as 9 mm and 12 gauge shotguns. Visual inspection of the site revealed very few intact projectiles in the soil. Projectile fragments were identified and found scattered throughout the site. The number found at this site was much smaller than expected based on the range's age and in comparison to other SAFR sites.

The Exploratory Soil Survey of Alaska conducted by the U. S. Department of Agriculture, Soil Conservation Service, lists the soil of ISC Ketchikan, Alaska as the order of Spodosols (USDA, 1979). Spodosols are mineral soils that have a spodic horizon--a subsurface horizon with an accumulation of organic matter and of oxides of aluminum with or without iron oxides. Spodosols form mostly on coarse-textured, acidic, parent materials which are subject to ready leaching. They occur only in moist to wet areas and are most common where it is cold or temperate. Forests are the natural vegetation under which most of these soils have developed.

Species low in metallic ion contents, such as pine trees, seem to encourage the development of Spodosols. As the litter from these low-base species decomposes, strong acidity develops. Percolating water leaches acids down the profile, and the upper horizons succumb to this intense acid leaching. The majority of this site could be described as a bog, with Muskeg soil. This soil is formed from the accumulation of sphagnum moss, leaves, and decayed matter resembling peat. It retains a high amount of moisture, has little strength, and compresses easily and substantially.

Integrated Support Command Kodiak

The USCG ISC Kodiak is located on Kodiak Island, Alaska (figure 6) and provides support for western Alaska. ISC Kodiak manages the largest area in the USCG, 21,000 acres. This large tract of military property on Kodiak Island has been occupied since the World War II Aleutian Campaign. Originally an Army Base, it has been a Naval Base and is presently a USCG Base. The Air Force has also been active on Kodiak Island where they built a tracking station at Chiniak after the war. As a USCG base, ISC Kodiak houses around 2,000 personnel and their families . The USCG is an integral part of the fishing industry, providing search and rescue and enforcement of international fishing law.

The law enforcement responsibilities of the 17th District requires USCG members to be qualified in the use of small arms. The SAFR at ISC Kodiak has historically been utilized for training purposes. The Kodiak SAFR is located in the Restricted Magazine Area, approximately seven miles southeast of Buskin Lake. Small arms training activities at the Kodiak range are conducted at an outdoor training facility having approximately 9-10 firing lanes with a berm constructed into the natural hillside. The berm is located beyond the firing lanes, serving to stop the forward progression of small arm projectiles. The exact age of this range is unknown, but it is thought to have been used for a number of years. It was estimated that 1,000 people train annually at the range with expenditures of approximately 100,000 rounds per year. When compared to other USCG SAFRs, the range at Kodiak is one of the more highly utilized ones. The type of munitions generally utilized at Kodiak's SAFR, according to site personnel, includes 9 mm, M-16, and 12 gauge shotgun.
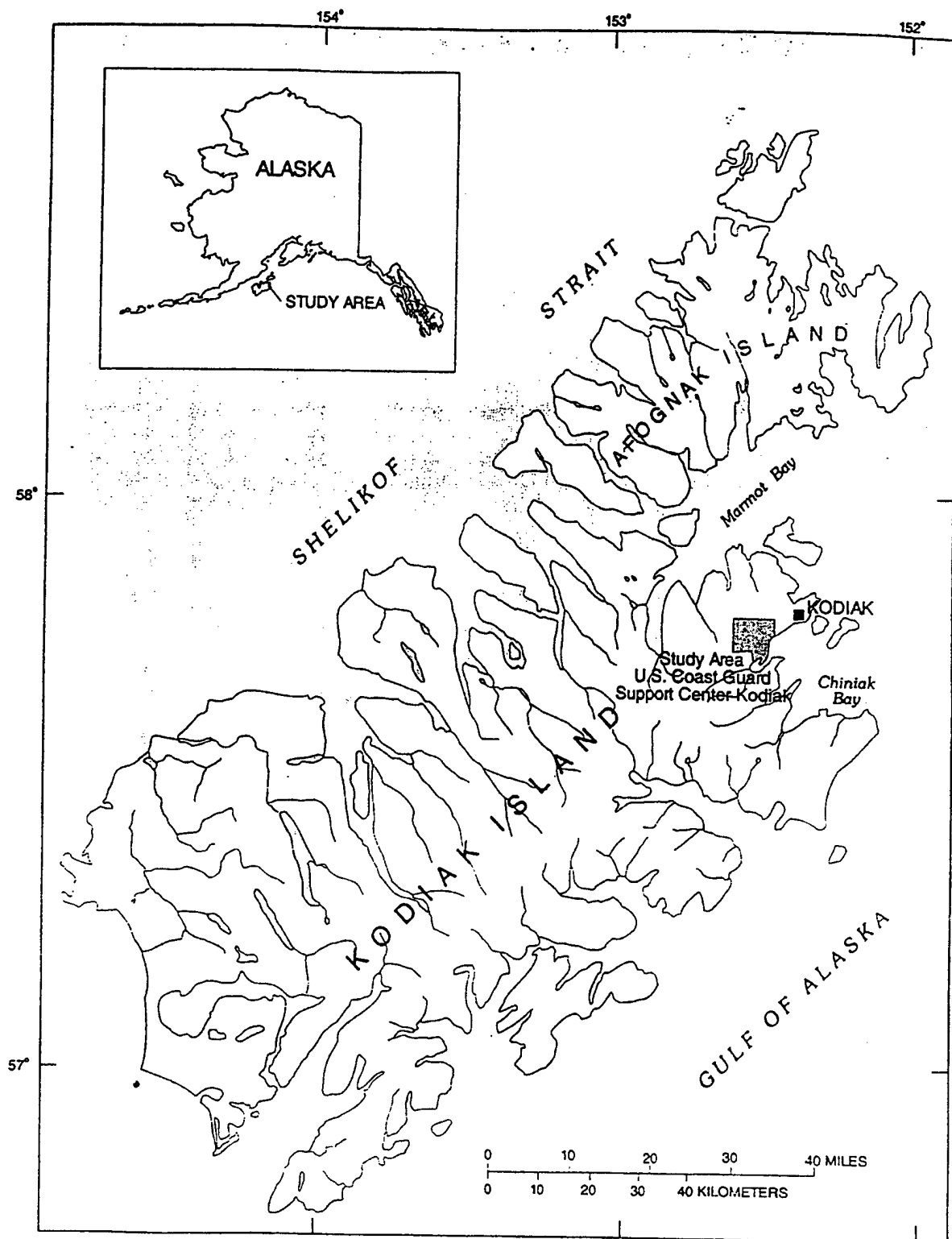
Figure 6. Location of Kodiak study area.

Site personnel at Kodiak also have expressed a desire to eventually construct a bullet trap at the range. The construction may involve earthwork and removal of the berm. Contaminated soil generated from such activities would require some form of disposal. This range is older, has a relatively high usage, and is located in an environmentally sensitive area. The soil description indicates that the soil is acidic, has little clay or organic matter, and is well drained (indicating a high permeability). These factors combine to elevate concern at this range and thus the requirement for inclusion of the Kodiak SAFR in this study.

The Kodiak, Alaska soil order, Andepts, is the Inceptisol soil formed on volcanic ash (USDA 1960). It is mostly dark brown to dark reddish brown. Soil particles range in size from cinders to clay. Many have buried surface horizons because of repeated deposits of ash. Volcanic ash from a 1960 volcanic eruption was observed near the surface of the Kodiak SAFR. Sites that were sampled indicated that there were two to five inches of brown organic soil; five inches and sometimes up to ten inches of white ash material; and, depending on the depth of sample collected, another three to eight inches of brown soil.

Training Center Cape May

The USCG Training Center at Cape May, New Jersey was established in 1948 when the USCG moved all East Coast recruit training facilities from Mayport, Florida. It is currently the home of the only basic training center within the USCG. In addition to the basic training activities, the Cape May facility also maintains operations which include: station Cape May, an aids to navigation team (ANT), an industrial support detachment (ISD), and five USCG cutters.

Cape May trains approximately 4000 military troops per year and is home to over 400 full time USCG personnel. Cape May is located at the southern tip of New Jersey (figure 7), and the training center is located on the eastern end of the peninsula formed by Cape May Harbor and the Atlantic Ocean. The training center covers 300 acres. The physical plant at the training center consists of approximately 90 buildings.

As part of the training activities at Cape May, the USCG owns and operates a SAFR. It is reported that this range has at least twice as much throughout as any other range operated by the USCG. The SAFR at Cape May is located at the southwestern tip of the USCG base. This SAFR is a semi-indoor range, which is now enclosed on all four sides. It has an exposed ceiling that has several overhead safety baffles. The floor of the range is composed of natural soil. The range is configured in a typical 25-meter range fashion consisting of 32 firing positions. The range is approximately 175-feet wide. In 1990 to 1991, a Caswell bullet trap was installed in front of an existing earthen berm. The bullet trap prevents bullets from impacting the soil behind the targets. Expended projectiles are routinely removed from the bullet trap and sent to a recycler. Shots that are fired short may penetrate the ground in front of the bullet trap but it is estimated that this is limited to only a small percentage of the rounds fired annually.

The old earthen impact berm behind the bullet trap is the area of concern for this study. This berm is approximately 175-ft long and stands approximately 20-ft high. The Atlantic Ocean is located approximately 200 feet behind the earthen berm. It is estimated that this berm was used from 1950 to 1990, or approximately 40 years of operation prior to the installation of the bullet trap. A conservative estimate for the number of rounds expended over the 40-year period is that

over 366,000 pounds of lead were deposited in the berm. This berm was sampled to determine the contamination characteristics of the Cape May SAFR, and bulk soils were also collected for study.
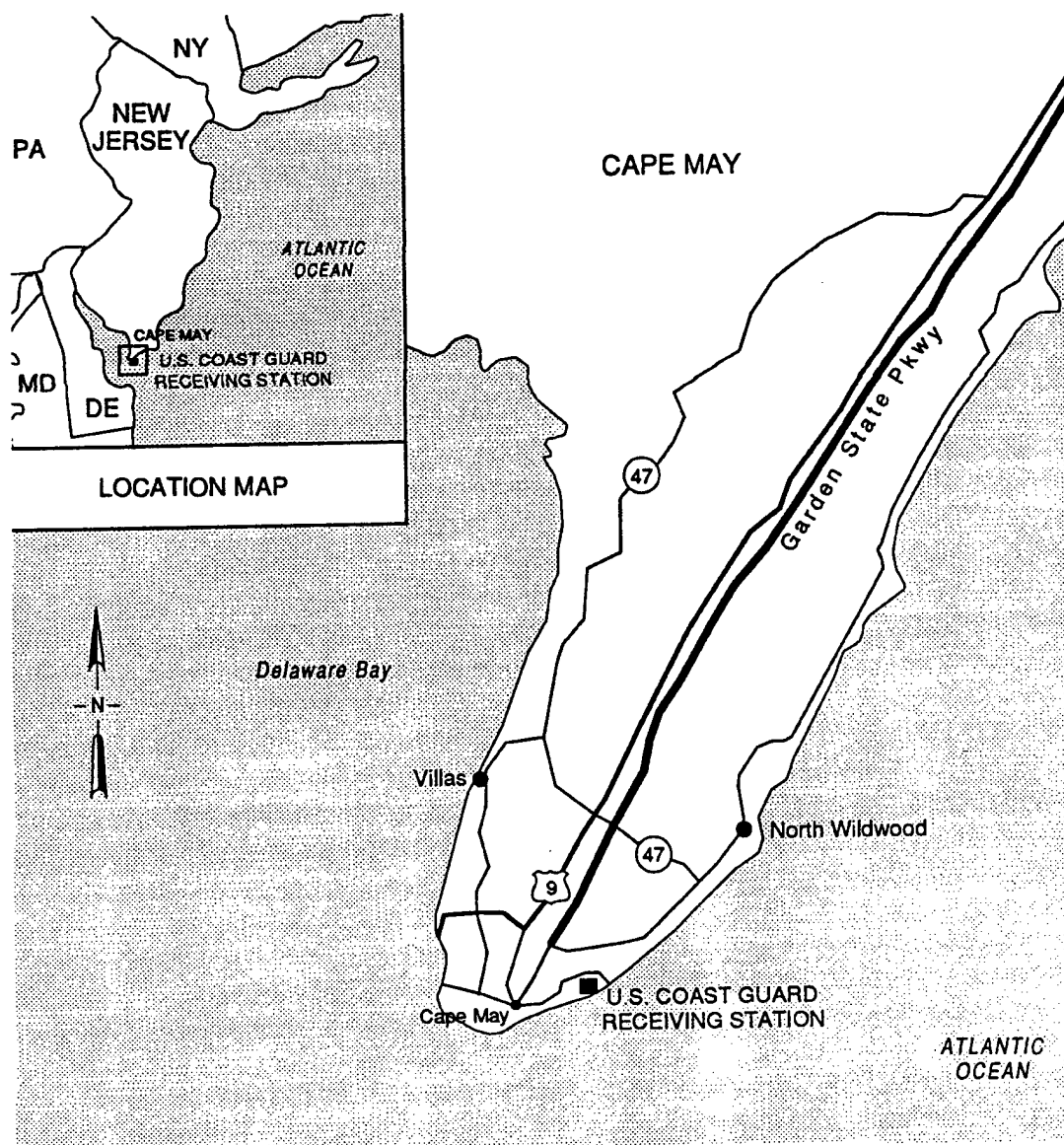
Figure 7. Location of the USCG Training Center, Cape May, New Jersey.

Cape May soil falls under the soil order Ultisols (Brady, 1990). Ultisols are soils with an argillic (clay) horizon and a low-base status (less than 35percent of the exchange capacity satisfied with base-forming metallic cations). Their mean annual temperatures at 50 cm depths are above 8°C. Most Ultisols have developed under moist conditions in warm to tropical climates. Except for the wetter members of the order, their subsurface horizons are commonly red or yellow in color, evidence of accumulations of oxides of iron. They are located mostly in regions of long growing seasons and of ample moisture for good crop production. The silicate clays of Ultisols are usually of the non-sticky type, which, along with oxides of iron and aluminum, assures workability. Most of the soils of the southeastern part of the United States fall in this order.

Udults (moist, well-drained Ultisols) extend from the East Coast to and beyond the Mississippi River Valley and are the most extensive soils in the humid southeast. Humults (high in organic matter) are found in the United States in Hawaii, eastern California, Oregon, and Washington. The USDA Soil Survey of Cape May, New Jersey shows that the Coast Guard SAFR soil is comprised of Fill Land, several feet in thickness (USDA, 1977). This fill material is quite sandy and infertile and has low available water capacity. Permeability is rapid, and the organic content is low. Unless topsoil is brought in, vegetation that is not tolerant to sandy, droughty sites is difficult to establish.

Communications Station New Orleans

The USCG Communications Station located in Belle Chase, Louisiana is located in the 8th District. While only limited information could be obtained regarding USCG activities at this facility, it was determined that prior to the operation of this facility as a USCG communication station, it was owned and operated by the US Navy as a weapons depot. In 1963, this area was transferred from Navy ownership to the USCG.

The USCG Communications Station is located southwest from the city of New Orleans on the west bank of the Mississippi River (figure 8). This USCG facility is relatively large, occupying approximately 2.5 square miles. The SAFR located at the USCG New Orleans facility is located northeast of the administration building. Site personnel report that this range was put into operation around 1976. Troops from sounding USCG activities as far as 100 to 150 miles utilize this facility for qualifying and training. It is estimated that approximately 120,000 rounds are expended at this facility annually. Weapons utilized at this range consist of 9-mm hand guns, M-16 rifles, and OO buck shot guns.

The SAFR is an outdoor range configured in a typical 25-meter range fashion consisting of approximately 12 firing positions. The range has a covered firing position where the shooters are initially stationed and weapons are loaded. This covered area has a concrete floor approximately 72-ft long and 45-ft wide. The majority of the range floor is composed of natural soil. The range also has overhead safety baffles to direct the path of the bullets. Expended projectiles pass through a target and are captured by an earthen berm located directly behind the target line. Railroad ties approximately three feet in height help retain the berm.

In 1995, the berm began to experience ricochet due to the large amounts of spent projectiles it contained. Because of this safety issue, the berm soil was excavated and placed in a waste pile located just to the southeast of the SAFR. The berm was reconfigured with soil consisting of Mississippi River bottom sediments. The soil pile is approximately 66-ft long, 123-ft wide, and 12-ft in height. Site inspection of the soil pile and berm indicated that only a few intact expended projectiles could be identified, although numerous bullet fragments were observed in the soil from both sources.

Soils in the Louisiana area are generally grouped into the soil order of Inceptisosls (USDA, 1904). The soil is associated with more advanced weathering and/or the accumulation of silcate, clay, iron, and aluminum oxides. Generally, large amounts of organic matter are absent.

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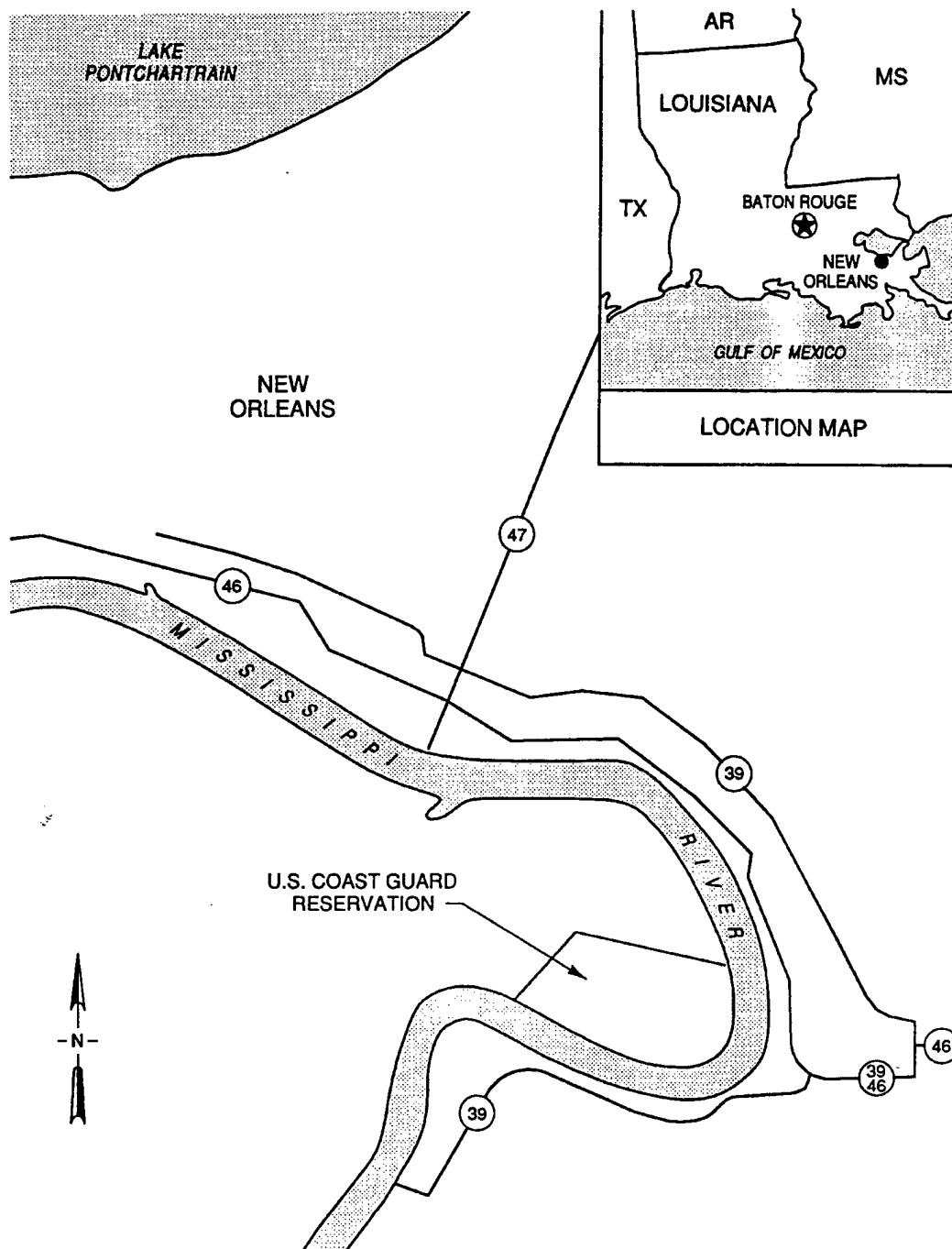
Figure 8. Location of the USCG Communications Station, New Orleans, LA.

Due to the proximity of the Mississippi River to the SAFR, soils at the range are believed to have originated from river deposits. These materials which are transported by the river are transported either by suspension or are rolled along the river bottom. Soil particles have the texture of fine sands or clays. They are largely composed of materials having mineral origins and have surprisingly small amounts of organic matter.

Treatment Alternatives

This report is not intended to provide a comprehensive review of treatment alternatives, which could be utilized to address metal contaminated soil, nor does it provide a review of cost issues associated with the implementation of such technologies. This section is presented to provide background information and a brief introduction of typical remediation technologies, which could be utilized at SAFRs.

Currently, a variety of treatment technologies exist for the remediation of heavy metal contaminated soils (Bricka et al., 1994). These technologies fall into four main categories: 1) physical separation/chemical processes, 2) thermal processes, 3) immobilization/ stabilization processes, and 4) vegetative uptake processes (Bricka, 1993). Many of the technologies are costly, are under developed, or have limited application. Technologies have been identified that could be utilized to remediate USCG SAFR soils at full scale. They include:

- No Action or Natural Attenuation
- Isolation Technologies
- Metal Immobilization Technologies
- Soil Washing Technologies
  - Physical Separation
  - Chemical Extraction
- Electrokinetic Technologies

This investigation focuses on those technologies that remove the contaminants from the soil, thus eliminating any health or environmental risk.

No Action or Natural Attenuation Alternatives

The "no action" alternative at USCG SAFRs would simply involve allowing the site to remain in its current state. While this option may present a cost-effective alternative, the risk associated with "no action" must be addressed. Addressing such risk assessment issues is outside the scope of this study, but the "no action" alternative should be evaluated as a possible engineering alternative when considering remediation.

Natural attenuation involves a slightly more proactive effort than "no action." With natural attenuation, no steps or only minor steps are taken to modify the existing site conditions. The primary difference between "no action" and natural attenuation is that with natural attenuation, the site is monitored to insure the environment has the ability to assimilate the contaminant with minimal impact.

Brady et al. (1998) proposed an eight-step protocol for demonstrating the natural attenuation potential of metal. While this protocol is still conceptual, it does highlight the data requirements to assess natural attenuation. This protocol includes:

1. Review available site data
2. Develop preliminary conceptual model and assess the potential for natural attenuation

3. If needed, perform additional site characterization to support natural attenuation
4. Update conceptual model
5. Simulate long-term behavior
6. Perform an exposure pathway analysis
7. If natural attenuation is acceptable, prepare long-term monitoring plan
8. Present results to regulators

Studies such as the one presented by this report supplement the data requirement of Step 3 (as presented above), and this data will directly support the efforts of Step 5. Brady et al. (1998) points out the usefulness of sequential extractions in predicting the mobility of metals. Without such data, the usefulness of natural attenuation cannot be assessed.

Isolation Technologies

Isolation technology involves reducing the environmental exposure of the contaminants. Such technologies involve a proactive approach that may be as simple as placing a clay (or asphalt) cover over the site to more complex treatments involving the addition of chemical reactants to the soil.

Metal Immobilization Technologies

Solidification/Stabilization (S/S) is an immobilization process that involves the mixing of a contaminated soil with a binder material to enhance the physical and chemical properties of the soil and to chemically bind any free liquid (USEPA, 1992). Solidification is generally described as the enhancement of the physical characteristics of the waste material. This is accomplished by reducing exposed surface area, which in turn lowers the convective transport of contaminants from the waste. Solidification usually entails the incorporation of the waste into a solid matrix or monolith. In comparison, stabilization involves the reaction of the waste's hazardous waste constituents with the S/S reagents to immobilize or otherwise contain them. The stabilization process may be as simple as the addition of lime or a sulfide source to a heavy metal liquid waste, or it may involve the development of special reagents specifically formulated to interact with the waste components. Most commercial vendors use a combination of solidification and stabilization to maximize the contaminant immobilization capability of the treated waste.

Several binder systems are currently available and widely used for the S/S of hazardous wastes (Cullinane et al., 1986). Typical binders include Portland cements, pozzolans, and thermoplastics. Most common S/S techniques are designed with either Portland cement or some type of pozzolan as the basic reagent. Portland cement is widely available, relatively economical, and well known to the general public as producing a very durable product. Pozzolans are siliceous materials that, when added to a source of lime, will go through a cementatious process similar to Portland cement, but at a much slower rate. Fly ash and blast-furnace slags are common pozzolans that are generally considered as waste materials themselves. Kiln dust is also a pozzolan and a waste material. Kiln dust is generated from the production of lime or cement. Although the quality of kiln dust varies, kiln dust generally contains enough lime and fly ash to set simply with the addition of water.

Soil Washing Technologies

Soil washing is a technology that reduces the environmental availability of the contaminants. Soil washing attempts to segregate the contaminants from the soil. The process of contaminant segregation actually involves two distinct processes: 1) physical separation of the contaminated and non-contaminated soil particles and 2) chemical extraction of the metal contaminants from the soil. The term "soil washing" may refer to physical separation, chemical extraction, or a combination of both. Physical separation and chemical extraction are discussed separately in the following sections.

Physical Separation Technologies

Physical separation is a process which attempts to separate the soil into various fractions by capitalizing on differences in particle size, density, surface properties, or other differing soil factors (Bricka et al., 1994). In general, particles with small diameters have the ability to retain or adsorb a greater quantity of metals per unit weight of soil because they have a larger surface area per unit mass available for metal bonding.

Physical separation processes are accomplished through several stages, typically beginning with an initial screening to remove large, oversized particles. The remaining fraction is further processed to isolate the finer fractions using a mechanical sieve or trammel screen. Particles that pass through the sieve or screen are further classified while the larger particles and removed for disposal or back-filling, depending on their level of contamination. Many unit operations are available for the physical separation of metal contained soil which are broadly categorized by the mining industry into comminution, gravity concentration, and flotation (Weiss, 1985).

This investigation focuses on mechanical screening, attrition scrubbing, and tabling as being representative of the physical separation processes. Each of these unit operations is briefly discussed below.

Mechanical Screening

Mechanical screening was investigated in this study using particle size analysis (PSA). PSA is a measurement of the size distribution of individual particles in a soil sample. The major components of PSA are the destruction and dispersion of soil aggregates by chemical, mechanical, or ultrasonic means and the separation of the particles according to size limits by sieving or sedimentation (Klute, 1986).

Attrition Scrubbing

Attrition scrubbing is used to remove superficially-bound contaminants such as adsorbed metal cations from solid particles. Attrition scrubbing is accomplished through the interaction of particles scrubbing against one another in a high solids environment. Two effects can be seen from attrition scrubbing on a bulk soil: scouring, and dispersion and disintegration. Scouring consists of the removal of coating or film from individual grains in a pulp (soil slurry) to produce fresh, clean grain surfaces. Dispersion and disintegration involve the breaking up of flocks or cementations and the sliming of the softer components (Allen, 1993 and Weiss, 1985).

It has been shown that a very strong correlation exists between decreasing grain size and the amount of heavy metal held by the soil fraction. As particle size increases, the amount of adsorbed metals decreases. This is largely due to the increase in surface area per mass of particle as the grain size decreases (Bricka et al., 1994). Recent research shows a strong correlation between total metals content and the <0.063mm fraction of the soil (Bricka et al., 1994).

Tabling

The wet concentrating table is a rectangular or rhomboid shaped riffled-deck operated in, essentially, a horizontal plane. A drive mechanism imparts a differential motion to the deck along its long axis while water flows by gravity along the short axis. The separation that occurs on a concentrating table is the result of numerous mineral processing principles simultaneously acting on the material feed to the table. These principles include flowing-film concentration, hindered settling, consolidation trickling, and asymmetrical acceleration (Weiss, 1985). Weiss (1985) and Wills (1992) give detailed descriptions of each of these principles.

Operationally, a slurry of solids and water is fed to the upper edge of the sloping table. As the suspended material moves across the table, it is caught and forms pools behind the longitudinal riffles. The differential shaking action of the table causes size classification and specific gravity stratification. This causes similar particles to arrange themselves vertically according to size (Weiss, 1985). A schematic of a shaking table with the idealized size and specific gravity stratification is illustrated in figure 9.
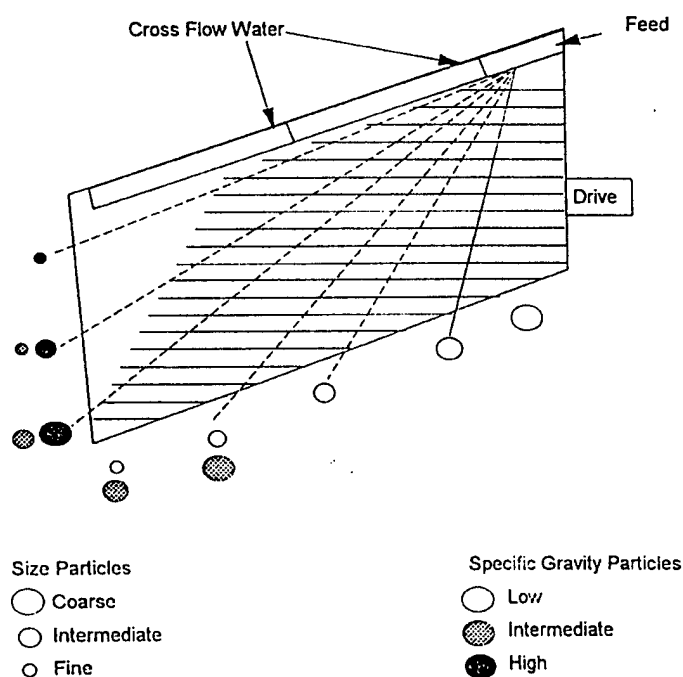
Figure 9. Map view schematic of particle separation for wet shaker table.

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The effectiveness and speed of the separation is dependent on the table's operational factors. These factors include: the size and shape of the particles, the difference in specific gravity of individual particles, the size consistency of the feed, the water and slurry flow rates, and the mechanical settings of the shaker table (Weiss, 1985).

Chemical Extraction Technologies

Chemical extraction is a process in which an extracting agent or solvent removes a metal contaminant from a soil particle. Generally, the soil is treated with a physical separation processing prior to chemical extraction to concentrate the metals and reduce the soil volume requiring chemical treatment. Thus, only the most heavily contained soil fraction is treated by chemical extraction. The soil particle may have the metal contaminant attached to the particle in a variety of ways. The metal may be attached to the soil surface, and/or the metal will be contained in the soils pore solution (Pryor, 1955). The metal contaminant may also be contained internally in the soil particle or attached to the surfaces of the soil particle's internal pores. Most contaminated soils have at least a small portion of the metal contamination contained internally, and this fraction may not be accessible for chemical extraction (Weiss, 1985).

Metal contaminants may be extracted from the soils using acids, bases, chelating agents, oxidizing and reducing agents, supercritical fluids, and in limited cases organic solvents. These extractants react with and solubilize the metals that are bound to the various fractions of the soil. Acids and bases generally rely on ion exchange to solubilize metals, chelating agents solubilize metals through complexation, and oxidizing and reducing agents target the solubilization of metals through a valence change. The application of chemical extraction technologies to soil can be applied using a number of methods. These can be grouped into three general categories: 1) dump or heap leaching, 2) percolation leaching, and 3) agitation leaching (Weiss, 1985). While these methods deviate in their approach, the main variables that are controlled generally include extraction solution, concentration of the extraction solution, extraction time, rate of agitation, and the number of stages (or extraction steps). Agitation leaching is one of the most aggressive extraction methods and will be the extraction method of focus for this study.

Agitation leaching is a process where the contaminated soil is slurried with the extraction fluid for a period of time (Oldshue, 1983). When equilibrium between the metal on the soil's surface and the metal contained by the solution is approached, the solubilization of the metal in the soil is slowed, and the extraction is considered to be complete. At equilibrium, additional metal will not be extracted from the soil's surface unless the soil is subjected to fresh extraction solution. Once the process is considered to be at equilibrium, the soil is separated from the extraction fluid using sedimentation, thickening, or clarification. The extraction process may be continued in a separate extraction vat with clean extraction solution to enhance extraction. An agitation vat coupled with a solid-liquid separation vessel (sedimentation or clarification) is considered to be a single stage (Mular and Bhappu, 1980).

Electrokinetics

Electrokinetic (EK) soil washing is a new and innovative technology that is perhaps one of the most promising in situ soil decontamination processes capable of removing heavy metals from

soils (Pamucka and Wittle, 1992). Figure 10 illustrates a theoretical EK remediation system. It is an in-situ process that may be used to treat both organic and inorganic contaminated soils. The research in this report focuses on heavy metal removal.
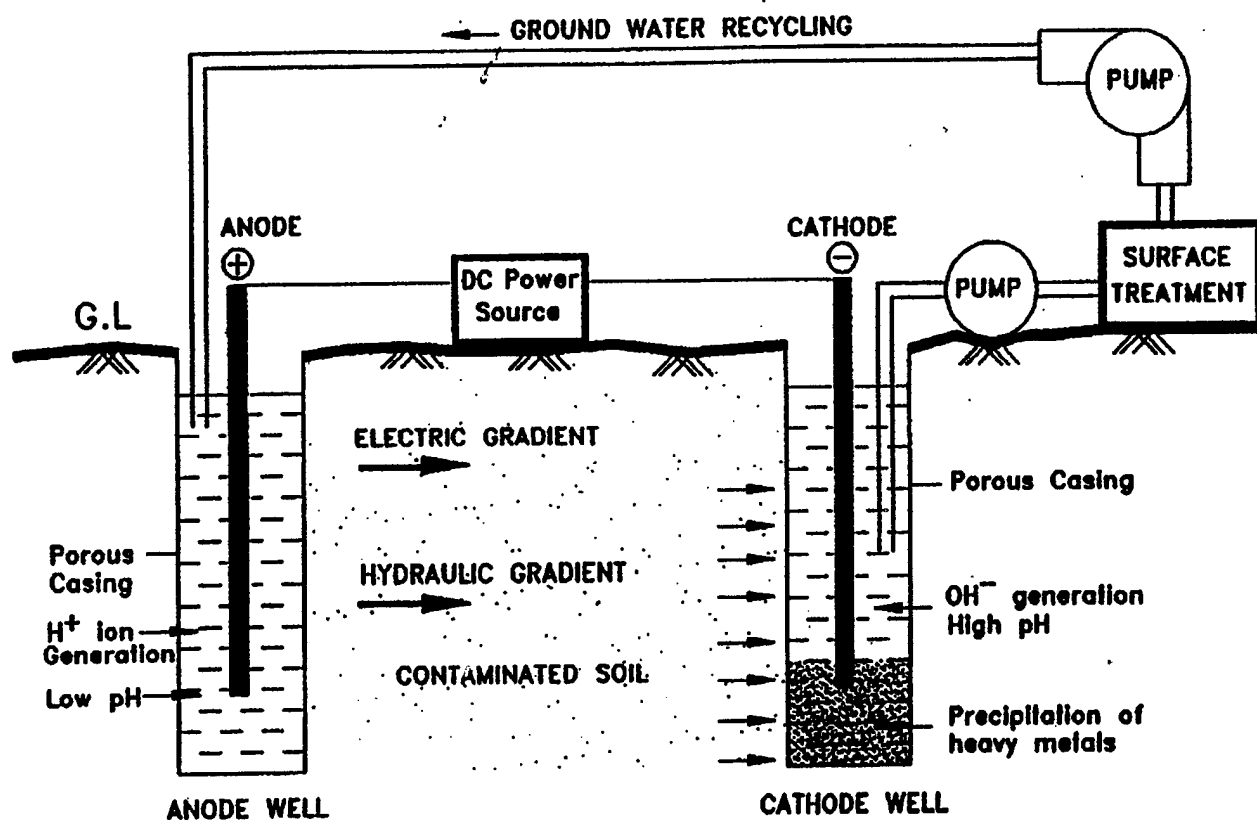
Figure 10. Conceptual field application of electrokinetic remediation of heavy metals (Khan and Alam, 1993).

Electrokinetic Theory

The first documented observation of electro-osmotic flow was reported by Reuss in 1808. Reuss observed the flow of pore water from the positively charged electrode (anode) to the negatively charged electrode (cathode). Since then, Reuss's observations have been used to develop a wide variety of engineering applications that benefit from the movement of pore water through soils. Casagrande (1952) was the first to incorporate electrosmotic water transport into practical applications. He used a closed anode and open cathode electrode configuration to increase the engineering strength of saturated clays through consolidation. Butterfield and Johnston (1980) reported that electro-osmotic flow could be used to increase the stability of metallic pile foundations. Chapell and Burton (1975) reported that electro-osmotic water transport could increase the stability of slopes by electrically extracting groundwater away from the slope surface. Recently, EK principles have been employed for environmental remediation of heavy metal contaminated soils (Alshewabkeh, 1994; Puppala, 1994).

Electrokinetic Phenomena in Soils

The physiochemical composition of clay particles in soils is the basis for EK phenomena. Clay particles generally have a net negative surface charge. The pore fluid has disassociated positive and negative ions in solution. The negatively charged surface attracts the positive ions (cations) in the fluid zone immediately adjacent to the clay surface. This forms a double diffuse layer (Mitchell, 1976), which gives rise to the EK phenomena.

EK phenomena includes four main components (figure 11): 1) electro-osmosis, 2) electrophoresis, 3) streaming potential, and 4) migration potential. Electro-osmosis is defined as the movement of fluid as a result of an applied electrical potential gradient with the electrical gradient acting as the driving force. Electrophoresis is defined as the movement of suspended solids in a fluid as a result of the application of an electrical potential gradient. Streaming potential and migration potential are basically the opposite of electro-osmosis and electrophoresis, respectively. Streaming-potential is defined as the electrical potential difference created as a result of fluid flow in soils, while migration potential is described as the electrical potential difference created due to the movement of suspended particles

Electrolysis Reactions

Due to the application of an electrical current in saturated conditions, electrolysis reactions (half-cell reactions) take place at the anode and cathode, respectively. Water is oxidized at the anode creating an acid (H^+) front while a base (OH^-) front is created at the cathode as the result of water being reduced. Oxygen and hydrogen are by-products of the anode and cathode reactions, respectively. The half cell reactions that take place in the anode and cathode are described by equations (1) and (2), respectively. Secondary reactions will occur that will affect species transport, but consideration of these reactions are beyond the scope of this research.

$$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \tag{2}$$

Subsequently, the acid and base fronts migrate towards the oppositely charged electrodes. Results have shown that the pH of the anode half-cell is reduced to below 2, and the pH of the cathode half-cell is increased to above 12 within 100 hours of treatment at a typical process current density (Acar et al., 1994).

Dissolution and Precipitation

Dissolution and precipitation of contaminants of indigenous soil minerals are the result of chemical reactions that occur during electrochemical treatment. These phenomena will have a profound effect on contaminant removal. The acid front produced at the anode will dissolve most heavy metals. However, the dissolution of different species depends on the pH of the soil pore fluid and the solubility product constant of each species (Alshewabkeh et al., 1994). Electrochemical processing of soils may also cause dissolution of clay minerals into elemental aluminum and silica. Such an effect can interfere or compete with heavy metal transport and removal.
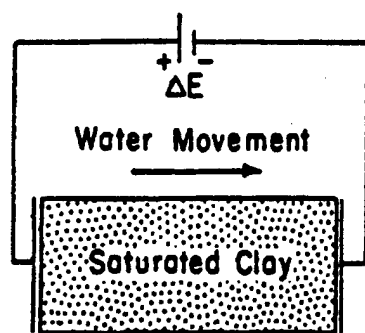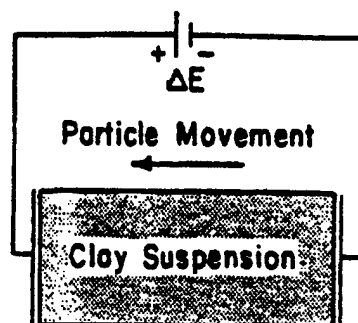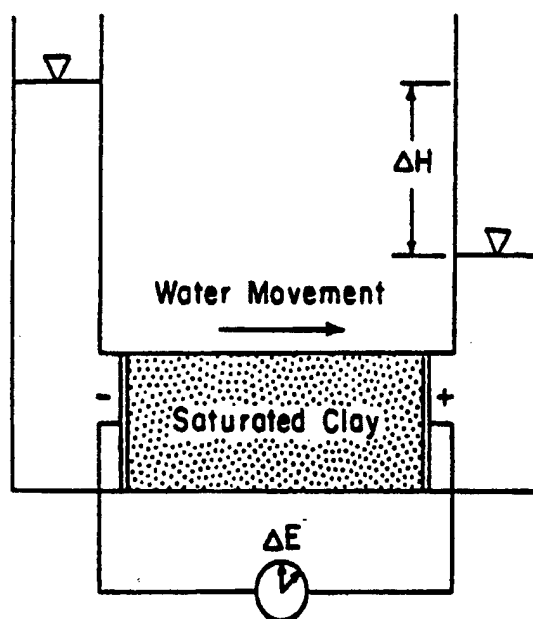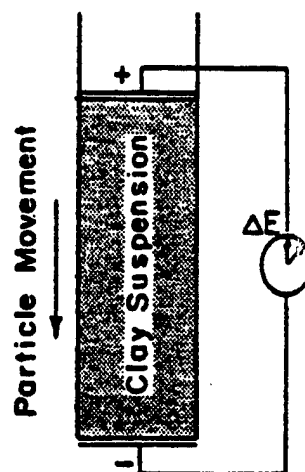
Figure 11. Electrokinetic phenomena in soils (Mitchell, 1976).

Precipitation of heavy metals and mineral salts will occur as a result of the base front created at the cathode. As the OH⁻ ion front migrates towards the anode, it reduces the soil and pore water pH of the system resulting in precipitation. This precipitation process can hinder electro-osmotic flow and, in effect, decrease metal removal efficiency. Precipitation of species, like dissolution, is also dependent of the solubility product constant of each species, as well as the pH of the pore fluid and the soil.

The transport of both fronts is a result of an electrical driving force created by the electrical potential difference applied across the soil. Advective forces also contribute to front migration, although to a lesser extent than that of the electrical driving force. The applied electric potential causes solubilized heavy metal ions such as lead, cadmium, and chromium (positively charged) to be transported to the cathode compartment, and negatively charged ions to be transported to the anode (figure 12).

a) Cation Transport Processes
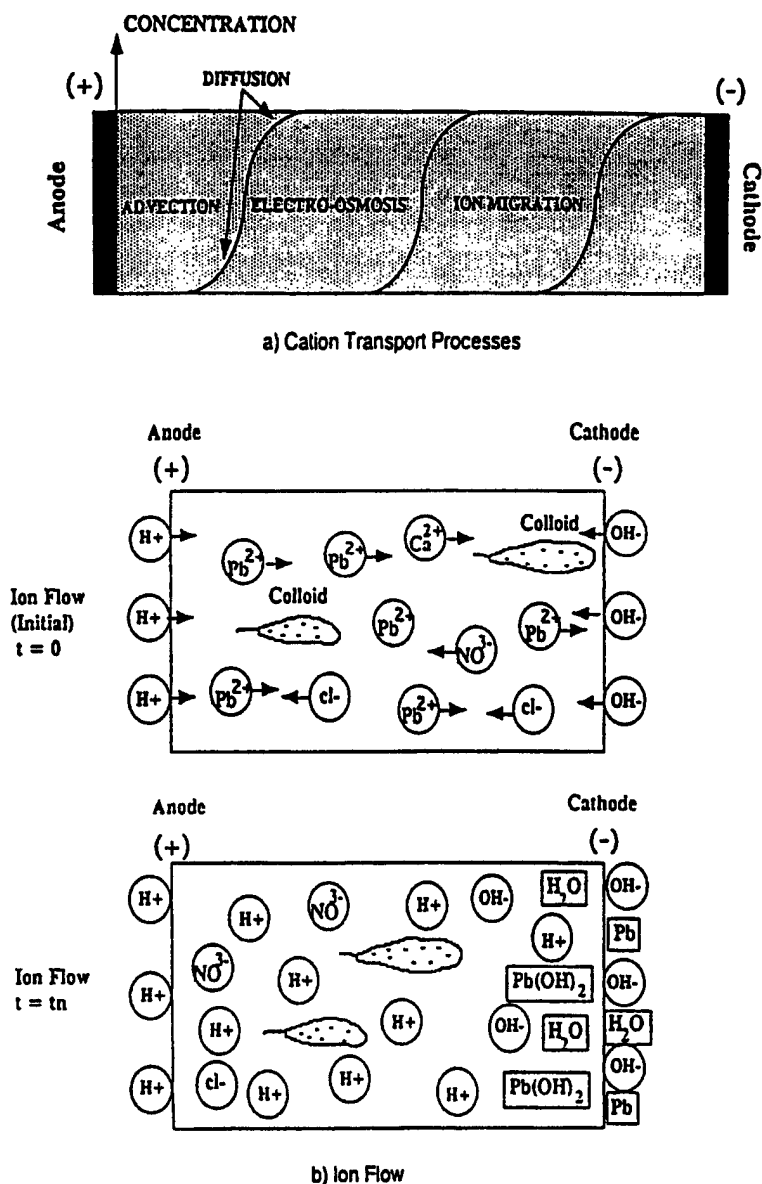
b) Ion Flow

Figure 12. (a) Cation transport processes and (b) ion flow in electrokinetic soil remediation (Hamed et al., 1991 and Acar et al., 1992).

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pH Control/Electrode Depolarization

Precipitation of many heavy metal ionic species will occur at high pH values and EK soil processing automatically raises the cathode pH due to the production of OH^- ions. These effects may make it necessary to buffer the cathode compartment to facilitate removal of contaminants (Acar and Alshewabkeh, 1993). By reducing the pH, precipitation of species that could clog the soil pore (transport) channels may be reduced or avoided. At the same time, depolarization of the cathode can be achieved which will result in the reduced production of OH^- ions. Cathode depolarization will also reduce power requirements and, subsequently, overall treatment costs by decreasing the electrical potential difference that applies across the soil mass (Acar and Alshewabkeh, 1996).

Materials and Methods

Overview of the Project

This investigation was conducted in five primary phases. These phases are briefly outlined below and are shown in flowchart in figure 13.

USCG SAFR Soil Study

↓

| Selection of USCG Sites to be Sampled |

↓

Collection of the Bulk and Core Soil Samples

Cape May   Kodiak
Ketchikan   New Orleans

↓

| Homogenization of the Bulk Samples |

↓

Characterization of the Bulk Soils

- Chemical Analysis
- TCLP
- Particle Density
- Buffering Capacity

↓

| Physical/Chemical Testing |

Particle Size Analysis   **Tabling**   **Chemical Extraction**   **EK**

Non-Attrition   Attrition   Non-Attrition   Attrition   Batch   CCME

- Cape May   └ Cape May   - Cape May   - Cape May   - Cape May   - Cape May
- Kodiak   - Kodiak   └ New Orleans - Kodiak   - Kodiak
- New Orleans   - New Orleans   - New Orleans - New Orleans

- Cape May
  Ketchikan
  Kodiak

Figure 13. Flow diagram of the USCG SAFR study.

Phase I: <u>Selection of the USCG Sites to be Sampled.</u> USCG facilities having SAFRs were contacted, and a determination was made as to the potential environmental risk the SAFR may

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pose. Sites were ranked, and four of the top sites were identified for sampling. These included Cape May, Kodiak, Ketchikan, and New Orleans.

Phase II: <u>Collection of the Bulk and Core Soil Samples.</u> Core and bulk samples were collected from the four sites by a sampling team from WES. These samples were shipped to WES for laboratory analysis.

Phase III: <u>Homogenization of the Bulk Samples.</u> Each of the bulk samples was separately mixed to produce uniform samples for testing. These mixed bulk soil samples were analyzed for metal content.

Phase IV: <u>Characterization of the Bulk Soils.</u> Homogenized bulk samples of soil from the four sites were subjected to characterization testing as shown in figure 13.

Phase V: <u>Physical/Chemical Testing.</u> Homogenized bulk soils were subjected to a combination of physical and chemical separation testing as shown in figure 13.

Sample Collection

Purpose of the Sample Collection

The WES sampling team's purpose for sampling the USCG SAFRs was not to identify the extent of contamination for regulatory purposes but to gain information that would support a better understanding of lead and other contamination at the SAFRs. The bulk samples collected would provide an indication of the contamination at these sites. A combination of core samples and bulk samples were collected for this purpose. All samples were collected, shipped, and evaluated in the WES's laboratories under chain of custody procedures. The bulk samples were collected from what was expected to be the area of heaviest contamination. This insured that the bulk soil samples would have a high probability of containing measurable concentrations of the range contaminants, but such samples generally represent a worst case contamination scenario.

Core Sample Collection

Core samples were collected from each of the four USCG SAFRs. At the Cape May, Kodiak, and New Orleans sites, core samples were collected using a model 77492 1-1/8 inch diameter sampling probe that was 24 inches in length. The sample probe was attached to a 10-pound slide hammer, and samples were driven into the soil by hand 24 to 28 inches. The probe was lined with a 1-inch polycarbonate sleeve. When the sleeve was removed from the sampler, the soil core remained intact inside the sample sleeve. Caps were placed over the sleeve ends to seal the soil core. The outside of the sleeve was then labeled, and the orientation was noted on the sleeve. A measuring tape was used to measure the depth of the sample hole, and this depth was recorded in the sample logbook. After the cores were collected, they were shipped to the WES for analysis.

At the Ketchikan SAFR, the soil had unique properties and, thus, required a different method of sampling. A detailed description of the Ketchikan sampling effort is presented by Teeter et al.

(1999a) and is briefly summarized below. The Ketchikan soil consisted of a peaty material commonly referred to as Muskeg. This highly organic soil prevented the use of typical core sampling equipment because the fibrous nature of the soil prevented sample retrieval. Many sampling techniques were tried, but the one that worked the best consisted of a fabricated sampler made from a six-foot section of thin-walled, 3-inch diameter pipe. A "T" slide hammer was used to drive the core sampler into the ground. After the sampler was removed from the ground, the sample specimen was extruded using a ramrod behind wadding that consisted of paper towels. The extruded samples were placed on aluminum foil, divided into three-inch sections using a knife, and placed into separate sealed plastic kitchen bags. As in the other sampling efforts, core samples were shipped overnight to WES for analysis.

Core samples were received by WES at the Hazardous Waste Research Center (HWRC) and were unpacked upon receipt. All samples were cross-referenced to the lab book to insure accurate accounting. Core samples were divided into three to four inch sections, and each section was placed in high-density polyethylene (HDPE) sampling container (except for the Ketchikan samples, which were divided in the field). All samples were thoroughly homogenized in the containers and stored for analysis. Prior to analysis, a 30g portion of the subdivided core soil sample was subjected to moisture analysis following the procedures as reported previously (Bricka et. al, 1992). Triplicate analyses were conducted to insure accurate moisture determinations, and all chemical results were reported on a dry weight basis.

Core Sample Analysis

Core samples were analyzed for the contaminants of concern (COC), lead and copper. In addition, zinc, chromium, and cadmium were also analyzed. Core and surface samples were digested according to EPA Method 3051 (USEPA, 1986) for solids. A Floyd® microwave digestion apparatus, model RMS-950, was utilized for sample digestions. The determination of the metal contaminant was accomplished using Perkin Elmer® Model 5100PC atomic adsorption spectrophotometer (AAS) with direct aspiration. The soils were extracted and analyzed for these five metal contaminants according to the method as listed in Table 5 (USEPA, 1992).

Table 5. Methods for the bulk sample metal analysis.

Contaminant of Interest	USEPA Digestion Method	USEPA Analytical Method
Cadmium	3051	7130
Chromium	3051	7190
Copper	3051	7210
Lead	3051	7420
Zinc	3051	7950

USEPA SW-846 (USEPA 1992).

Bulk Sample Collection

Bulk samples were collected using a standard shovel, and the samples were placed in five-gallon plastic buckets. Bulk sample sites were selected where soil contaminant concentrations were believed to be high, based on site observations. Sample collection was performed by marking

off a small area. The vegetation was removed from the surface prior to sample collection. Samples were collected to a depth that equaled the length of the spade portion of the shovel or just slightly deeper (approximately 12 to 14 inches). Using a shovel, the soil was mixed in the excavated area and placed into buckets. The sample buckets were labeled, recorded in the lab book, and prepared for shipment after filling. These bulk samples were used for all Physical/Chemical Testing.

Bulk Sample Homogenization

The purpose of homogenization is to obtain a uniform soil sample so that the results generated in different tests can be compared. Each of the soils was subjected to the homogenization procedure described below.

Each bulk soil sample was homogenized separately. The entire sample from each bulk sampling site were weighed using an AND®, model FV-150KA1, digital floor scale and then emptied into large shallow plastic containers for easy handling. The soil was mixed manually by turning with a shovel. Sub-samples were collected for initial moisture and lead analysis. A Denver® Moisture Analyzer, model 9200207.1, was used to perform the moisture analysis. Lead analysis was conducted according to the methods presented in table 5. The soil was allowed to air dry for approximately three days in the shallow plastic containers. During the air drying process, the soil was turned frequently, and the large clumps of soil were broken into smaller-size pieces.

After the bulk samples were dried, they were each passed through a mechanical sieve for separation of the large rocks and oversized lead particles from the bulk soil. A Sweco® 30-inch diameter mechanical sieve, model number XS30S6666, fitted with 6.35 millimeter (mm) aperture screen was used for separation. The 6.35 mm size fraction was removed from the top screen, placed in five-gallon plastic containers, and stored for later investigations. The < 6.35 mm soil fraction which passed through the sieve was utilized for the majority of the subsequent experiments. After the soil was sieved, the < 6.35 mm soil was passed through a Gilson® model SP-Z sample riffler using a series of three passes to produce a thoroughly homogenized soil. Upon completion of the riffling, the samples were re-weighed and placed in five-gallon containers, which were stored at 4°C to await further testing.

Characterization of the Bulk Soils

Bulk Chemical Analysis

After being thoroughly homogenized, the bulk soils from each site were screened for the COC, Pb and Cu. In addition, Zn, Cr, and Cd were also measured. The soils were extracted and analyzed for these five metal contaminants according to the method listed in table 5.

TCLP Analysis

The toxicity characteristic leaching procedure (TCLP) is the leaching procedure that the US Environmental Protection Agency (USEPA) utilized to determine if a material should be classified as a hazardous waste (USEPA, 1986). Bulk soils were subjected to the test to

determine if lead (the only TCLP listed metal found in bullets) in the TCLP leachate exceeded 5 mg/l. The TCLP method outlined by the USEPA (USEPA, 1986) is briefly summarized below.

This method consisted of crushing the soil sample after drying to pass a 9.5 mm standard sieve. This crushed sample was placed either in a 0.5 M acetic acid extract or an acetate buffer extract, depending on the buffering capacity of the soil, at a 20:1 liquid-to-solid ratio. The soil and extract were tumbled end over end for 18 hours. The sample was filtered using a Whatman GF/F 0.75 μm filter at the completion of this period. The filtered extracts were placed in precleaned bottles and stored at 4°C prior to analysis. These extracts were analyzed according to the methods listed in Table 5.

Buffering Capacity

Experiments were conducted on bulk soils from the four SAFR sites to determine the buffering capacity of the <6.35 mm soil. A Metrohm™ 670 Titroprocessor was used to conduct buffering capacity of the soil samples, using an acid addition procedure following the manufacturer's guidelines, as described as follows. First, a program to control the rate of titrant addition was entered into the titroprocessor's memory. Two to five grams of oven-dried soil were then weighed on a Sartorius model 210 analytical balance to 0.001 g accuracy and electronically entered directly into the titroprocessor's memory. The soil sample contained in a 250 ml glass beaker was slurried with 100 ml water. The slurry was rapidly mixed for approximately 25 minutes. After this period of rapid mixing, the rate of mixing was reduced and the Brinkman™ combination pH-glass electrode Metrohm model 6.0202.102 and the titrant addition tube were inserted into the slurry, and the titrator was started. The titrations were carried out using a 0.02 molarity (M) solution of nitric acid. The titrant was added at a rate of 0.2 ml/min and proceeded until the stop parameters in the program (end points = 8, Titrant Volume = 60 ml, or pH<2) were reached or until the titration curve exhibited a horizontal straight line, which indicated that all the species in the soil slurry were completely neutralized. The volume of acid added versus the pH was automatically plotted by the titroprocessor.

Particle Density Analysis

Soil particle density refers to the density of solid particles collectively, or to the ratio of total mass of the solid particles to their volume, excluding pore spaces between particles (Klute, 1986). Published data indicates that, on an average, soil has a particle density range of 2.45-2.80 g/cc (Brady, 1990). A significant deviation from this range may give insights to the treatability potential of a contaminated soil using physical separation methods. Particle density analysis was conducted on the <6.35 mm bulk soils of all four SAFRs.

All particle densities were determined using a Micromeritics AccuPyc® 1330 Pycnometer. Approximately two to five grams of the bulk sample were added to the sample cup of the pycnometer, and the analysis was initiated. This fully automatic gas displacement pycnometer collected the data, performed the calculations, and displayed the results as g/cc. Triplicate analysis was performed for each sample, and an average was reported.

Particle Size Assay

The pre-sized bulk soils (<6.35 mm) from three of the four SAFRs were subjected to particle size assay (PSA). Soil collected from the Ketchikan SAFR could not be processed through the seives due to its fibrous nature and, thus, was not subjected to PSA. Soils were subjected to a particle size assay to determine the partitioning of metals in each of the soils through wet sieving analysis. The soils were wet sieved into seven fractions as shown in table 6.

Table 6. Soil sieve size fractions.

Sieving Order	Sieve Size	Soil Fraction
1	2.0 mm	6.35 mm - 2.0 mm
2	1.0 mm	2.0 mm - 1.0 mm
3	0.5 mm	1.0 mm - 0.5 mm
4	0.25 mm	0.5 mm - 0.25 mm
5	0.125 mm	0.25 mm - 0.125 mm
6	0.063 mm	0.125 mm – 0.063 mm
7	------	<0.063 mm

Wet sieving consisted of taking approximately 1200 grams of moist, <6.35 mm homogenized soil and passing it through a 2.0 mm US standard sieve until the process water passing through the soil was essentially clear. The soil was then gently worked over the screen in an attempt to deagglomerate the fine grain particles from the coarse grain particles. Process water, used to wash the soil retained on the screen, was passed through the next sieve (1.0 mm). This process was repeated until the soil was passed through a set of six Gilson® 12 inch stainless steel sieves as shown in table 7. The soils retained on the sieves and the process water passing through the 0.063 mm sieve were collected. The soil and process water containing the <0.063 mm soil fraction were de-watered using a custom-made air pressure filter. The pressure filter utilized Sharkskin® filter paper with an average pore size of 8-12 m. The maximum pressure used to filter the samples was approximately 80 psi. The pressure filter produced a filter cake that was further de-watered by drying the soil cake in a VWR®, model 1370G, vented oven at 104°C for 24 hours. After the soil cakes were dried, they were weighed and stored in plastic bottles. Each fraction was analyzed for COC and subjected to TCLP analysis as previously described.

Attrited Particle Size Analysis

Bulk samples were also subjected to attrition scrubbing. However, there was only a small amount of Kodiak and New Orleans soil available for testing, so these soils were not subjected to attrited PSA testing. The Ketchikan soil, as explained previously, was very fibrous and, thus could not be attrited. Therefore, only the Cape May soil was subjected to attrition analysis. Details of the attrition procedures are discussed below.

The attrition test was performed in a WEMCO® Laboratory Attrition Scrubber fabricated with a high-torque variable speed drive motor and a stainless steel shaft. The variable speed drive is adjustable in the range of 650-1900 RPM, and speeds are read directly from a tachometer. The attrition apparatus consists of three bladed impellers and a closely fitted stainless steel tank with a lid. The impellers are fabricated into one piece with all the blades facing at opposing pitches and are attached to the end of the shaft. This type of configuration maximizes the particle to particle contact that produces the desired scrubbing action.

Attrition scrubbing performance is generally studied by varying a number of parameters, including solids density, impeller speed, residence time, and surfactant use. A typical testing matrix (Freeman et. al, 1993) is presented in table 7. A modified version of this testing matrix was used in this study. The attrition scrubbing performed for this study consisted of a single test per soil using the highest solids density, the fastest speed, the longest residence time, and no surfactant addition. This method provides information on whether attrition scrubbing is feasible for a particular soil, while minimizing the test matrix.

Table 7. Typical attrition scrubbing test matrix.

	rpm=900								Solids=75%							
	60% Solids				75% Solids				900 rpm				450 rpm			
Time, minutes	1	5	10	15	1	5	10	15	1	5	10	15	1	5	10	15
Soil n,	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
With Surfactant	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
W/O Surfactant	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

To obtain optimum effectiveness of the WEMCO® Laboratory Attrition Scrubber, a regulated volume of soil must be added to the stainless steel tank. The manufacturer recommends that the tank be filled with material to the underside of the upper blade. The actual weight of the sample added is dependent on the bulk density of the soil.

Approximately 1200 grams of moist <6.35 mm homogenized soil were placed in the attrition scrubber's stainless steel tank. The appropriate amount of water was added to the soil to produce a 75 percent to 80 percent solid slurry. The speed was set to approximately 1100 RPM, and the slurry was attrited for 15 minutes. These operational parameters were based on the modified test matrix previously described. These soil samples, after attrition, were subjected to the PSA analysis as described above. Each fraction generated from the attrited particle size analysis was subjected to total metal analysis for the COC and TCLP.

Wet Shaker Tabling Analysis

A Wilfley Laboratory Concentrating Table, otherwise known as a wet shaker table, was chosen for use in the tabling analysis experiments. The Ketchikan soil was not subjected to tabling analysis due to its fibrous nature. Tabled samples were subjected to the chemical testing for COCs and TCLP as previously described.

Shaker Table Equipment

There are two basic types of table decks: sand decks and slime decks. Sand decks are characterized by deep, extensive riffles, necessary to effectively process coarser size material. Slime decks are characterized by shallow riffles to minimize the disturbance in a bed of fine particles and still allow the cascading of materials necessary for removing low density particles (Weiss, 1985).

The shaker table experiments conducted in this study used a Wilfley Laboratory Concentrating Table with a model 13A Sand Deck. The differential shaking motion is provided by a gear connected to a pulley that is driven by an electric motor. The table deck, gearbox, and the pulley-motor system are mounted in line. A trough with multiple sample points is also attached to the table mount. The deck and sampling ports are made of polyester resin reinforced fiberglass material. The table deck size is 18 inches by 40 inches and has a maximum capacity of 2.5 lb/min of solids throughput. While this piece of equipment is large enough to simulate pilot scale, it is still small enough to run batch/bench scale experiments.

Optimization of the operating parameters is essential to achieve the maximum performance of the Wilfley Concentrating Table. Previous studies indicate that the feed soil particle size range should be between 2.00-0.063 mm. The presence of large volumes of fine soil particles (<0.063 mm) on the table slows the sizing and specific gravity stratification and, hence, the efficiency of the separation (Weiss, 1985). For optimum performance, the manufacturer suggests using a feed soil that contains less than 5percent of fine material with the 13A Sand Deck.

Preliminary runs on the table indicated a slurry flow-rate range of 0.5-0.75 gal/min of a 20 percent solids mixture. This translates into approximately 0.70-1.41 pounds of solids/min, which is well below the recommended maximum of 2.5 lb/min for this table. The cross water flow-rate was determined to be 1.0 to 2.0 gal/min in the pretests, using the previously specified solids throughout. The differential shaking motion is defined by the speed and stroke of the table. These parameters are adjusted based on table feed properties. If the feed is coarse, a long stroke and slow oscillation is recommended, typically a speed of 230-285 rpm and a stroke ranging in length from 1-1/4 to 3/4 inches. If the feed is fine, short strokes and high oscillations are preferred, typically 285 to 325 rpm for the speed and a 3/4-3/8 inch stroke length (Carpco, 1993). The final adjustable parameter table slope should be minimized to obtain sample distribution across the table while maintaining cross flow (Weiss, 1985).

Shaker Table Test Method

Prior to the initiation of the shaker table tests, the <6.35 mm soils were pre-sized to obtain the recommended table feed particle size range of 2.0-0.063 mm. The pre-sizing was accomplished by wet sieving to remove the >2.0 and <0.063 mm particles. It was determined through pre-testing that approximately 2500 grams of dry pre-sized feed was needed to conduct each tabling experiment.

The pre-sized soil was slurried to a 20percent solids mixture and fed to the table. Table feed rate, cross water flow, table tilt, speed, and stroke were adjusted to obtain proper separation based on visual inspection. Table 8 gives a listing of the actual parameters used in both the attrited and non-attrited experiments.

Table 8. Shaker table experimental operating parameters.

Experiment	Amount of Dry Pre-sized Feed (g)	Feed Solids (%)	Feed Slurry Flow Rate (gal/min)	Feed Solids Flow Rate (lb/hr)	Cross Water Flow Rate (gal/min)	Table Tilt (degrees)	Speed (rpm)	Stroke (inches)
Non-Attrited	2539	20	0.5	1.0	1.5	96	281	3/8
Attrited	2635	20	0.5	1.0	1.5	96	281	3/8

Proper separation was determined by observing distinct bands of material at the right end of the table deck. Once distinct separation bands were observed for several minutes and the adjustable parameters were fixed, the process was determined to be at "steady state" and ready for sampling. The "bands" of material flowing off the table were isolated by "cutters" placed on the table's trough edge. These sample "cutters" consisted of a downward sloping piece of polyester resin reinforced fiberglass which directed the flowing bands of material into separate collection ports along the trough. The separated bands of material flowed through the appropriate sampling ports and were collected in five-gallon containers as product. All of the feed in the tank was processed on the table to insure a sufficient amount of product. Tabling separated the pre-sized feed into three fractions: concentrates (cons), middlings (mids), and tailings (tails). The particles with the highest densities are typically associated with the cons fraction and are discharged at the left end of the table. The tails fraction particles that usually contain the lightest density are discharged at the bottom-right side of the table. The mids fraction typically consists of medium density particles and is discharged at the bottom-left end of the table. These are terms commonly used in the mining industry and have been adopted for use in this study. The three tabling products (cons, mids, and tails) collected during these tests were de-watered as previously described. The dry soils were analyzed for COC and TCLP constituents as described previously.

Attrited Wet Tabling Analysis

Bulk samples were also subjected to attrition scrubbing followed by wet tabling analysis. However, as explained earlier, only limited Kodiak soil was available for testing, thus, this soil

was not subjected to attrition testing. Cape May and New Orleans soils were subjected to attrition analysis by tabling. Attrited wet tabling analysis consisted of attriting the soil as described under the PSA section of this report. This attrited soil was tabled as described above. The dry soils were analyzed for COC and TCLP constituents as described previously.

Soils Chemical Extraction Evaluation

Batch extraction studies and pilot-scale chemical extraction tests were conducted on three of the USCG SAFR soil samples (Cape May, Kodiak, and New Orleans). Ketchikan soils were not subjected to chemical extraction studies. In the batch extraction studies, soils from the New Orleans waste pile and impact berms were utilized. Figure 14 presents a flowchart outlining the test conducted for the extraction study.
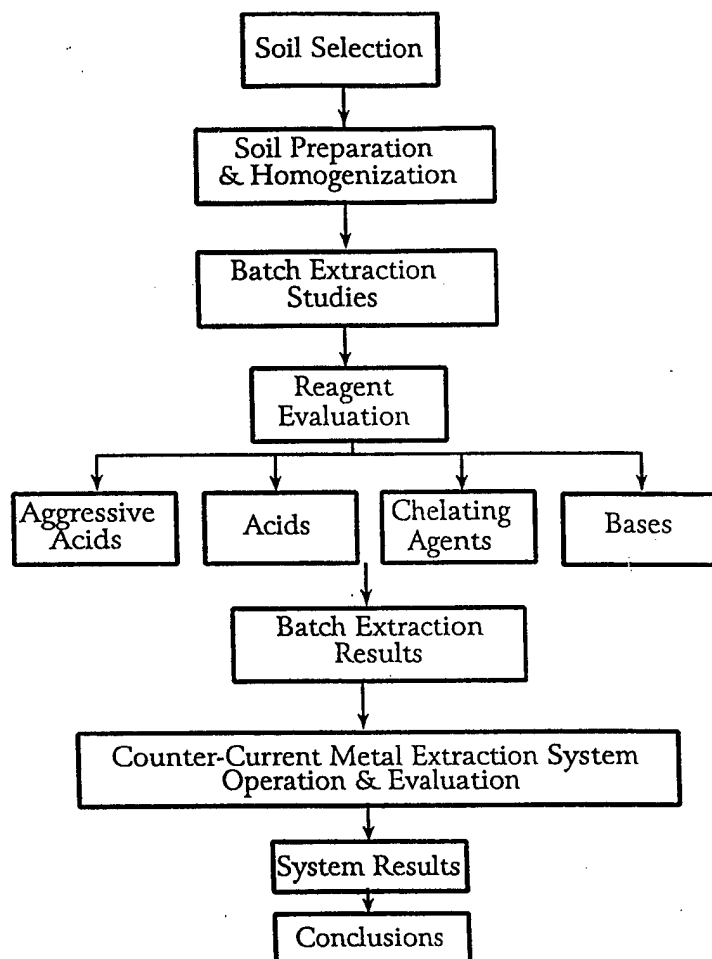
Figure 14. Flowchart of the chemical extraction study for the USCG soils.

Batch Extraction Studies

Soil and Solution Preparation for Batch Extraction Studies

The bulk soils were dried and homogenized using a Gilson® Sample Riffler. The bulk samples were sieved to less than 2 mm, and a sub-sample of approximately 300 grams of soil was drawn from the less than 2-mm fraction for use in the batch extraction studies. After further drying of the 300-gram sub-samples, the soils were ground into a powder using a mortar and pestle to aid in homogenization and to accelerate the equilibrium extraction procedure. Solution preparation consisted of dissolving American Chemical Society (ACS) grade crystalline or concentrated forms of acids, chelating agents, and base in de-ionized distilled water. Batch testing consisted of extracting the soil samples using ten reagents at three concentrations. A total of 120 extractions were conducted in the batch extraction tests. The reagents and concentrations used in the batch extraction studies are shown in table 9.

Table 9. List of chemical reagents and concentrations.

Chemical Reagent	Concentration of Solution		
HYDROCHLORIC ACID (HCL)	0.01 M	0.05 M	0.1 M
Nitric Acid (HNO_3)	0.01 M	0.05 M	0.1 M
Phosphoric Acid (H_3PO_4)	0.01 M	0.05 M	0.1 M
Sulfuric Acid (H_2SO_4)	0.01 M	0.05 M	0.1 M
Citric Acid	0.01 M	0.05 M	0.1 M
Gluconic Acid	0.01 M	0.05 M	0.1 M
ETHYLENEDIAMINETETRA-ACETIC ACID (EDTA)	0.01 M	0.05 M	0.1 M
Diethylenetriamine-Pentaacetic Acid (DTPA)	0.01 M	0.05 M	0.1 M
NITRILOTRIACETIC ACID (NTA)	0.01 M	0.05 M	0.1 M
Sodium Hydroxide (NaOH)	0.01 M	0.05 M	0.1 M

It should be noted that both HNO_3 and HCl are aggressive mineral acids and can actually destroy the matrix of the soil if applied in high concentrations. Matrix destruction may leave the soil unsuitable for vegetation if additional treatment is not applied to the post treated soil. Citric acid, EDTA, DTPA, and NTA are chelating agents that are relatively harmless to the soil structure; however, NTA is a suspected human carcinogen and may not be suitable for field use. NaOH is a strong base that will be used to investigate the solubilization of the heavy metals in a high pH environment. Heavy metals are generally amphoteric in nature and can be solubilized in either highly acidic or highly basic environments.

Baseline Metals Analysis

The baseline metals concentration in each of the soils was determined prior to extraction testing. To aid in reproducibility, samples from each of the selected soils were thoroughly mixed prior to analysis. The samples were digested according to EPA Method 3051 (USEPA, 1992) entitled "Soil Sample Digestion For Floyd® Digestion Vessels." Total metals samples were analyzed using a Perkin-Elmer®, Model 5100PC AAS according to the methods shown in table 5. Each sample was digested and analyzed in triplicate, and an average was taken to determine the total metal content of each sample.

Batch Extraction Testing

Two grams of each soil sample were weighed using a Mettler top-loading balance having +/-0.02-g accuracy and placed in a 50 ml polypropylene copolymer (PPCO) Oak Ridge® centrifuge tube. A solid-to-liquid ratio of 0.05 was used as determined in previous studies (Neale, 1995) where 40 ml of the extracting agent were added to the 50 ml centrifuge tube containing the soil. Each of the samples was placed in an end-over-end tumbling apparatus operating at 18+/-2 rpm for 30 hours to insure that chemical equilibrium was established (Neale, 1995). After tumbling, the samples were placed in a Sorvall® Superspeed SS-3 tabletop centrifuge. Each sample was centrifuged for 30 minutes at approximately 15,000 rpm after which the liquid portion of the sample was decanted into a clean 125 ml Nalgene® HDPE bottle. The concentrations of dissolved COCs in each sample were determined as previously described.

Counter Current Extraction Pilot Tests

Design and Construction of Chemical Extraction System

A pilot-scale counter-current metal extraction (CCME) system was designed and constructed to simulate large-scale chemical extraction systems. Figure 15 is a detailed schematic of the pilot-scale system, which consisted of four identical sets of reactors and clarifiers that were designed by WES and specially constructed for the WES by Ace Glass, Inc. of Vineland, New Jersey. System flow was regulated utilizing two identical digitalized console pump drives supplied by Cole-Parmer Instrument Company (Model No. G-07523-30). These drives, each with a maximum flow-rate of 380 ml/minute, held four Masterflex® Easy-load L/S pump heads (Model No. 7518-02). One drive was used to control the flow of the initial fresh (contaminated) soil slurry and fresh (uncontaminated) extracting agent solution, while the other drive pumped the underflow slurries from clarifiers in each of the four stages to reactors in the previous stages. During operation, the fresh slurry was introduced into the fourth stage reactor and was eventually pumped up to the first stage reactor while fresh extracting solution was introduced into the first stage reactor, and the spent extraction fluid eventually exited the system via the fourth stage clarifier. Thus, true counter-current flow was achieved.

Each reactor (Model No. QC617-1) held approximately two liters of slurry and contained four baffles that were designed to insure that complete mixing of the soil slurry was achieved. Each clarifier (Model No. QC617-3) held approximately two liters of slurry and was equipped with two three-fourths-inch inlets and two, three fourths-inch outlets. The two inlets were connected

to the reactor outlets using three-fourths inch Tygon® tubing. The clarifier bottoms were angled to allow solids to move more easily to the bottom outlet of the vessel while the less turbid extracting fluid remained near the top of the clarifier. Each of the four reactors was equipped with a Lightnin'® L1U08F Labmaster variable speed mixer with 30-inch shaft (Model 310 Impeller) that delivered a maximum mixing speed of 1800 rpm. The mixers insured adequate contact between the soil slurry and extracting agent. A 200-liter Nalgene® tank was used to store the fresh soil slurry. The slurry was mixed using a Lightnin'®, Model XJ-30VM variable speed mixer with a nine-inch diameter impeller. The extracting agent solution was prepared in a 200 liter Nalgene® tank and mixed using a Lightnin'® Model CS-LB566 single speed mixer. Two hundred liter Nalgene® tanks were also used to hold both the soil and extracting agent effluents from the system.
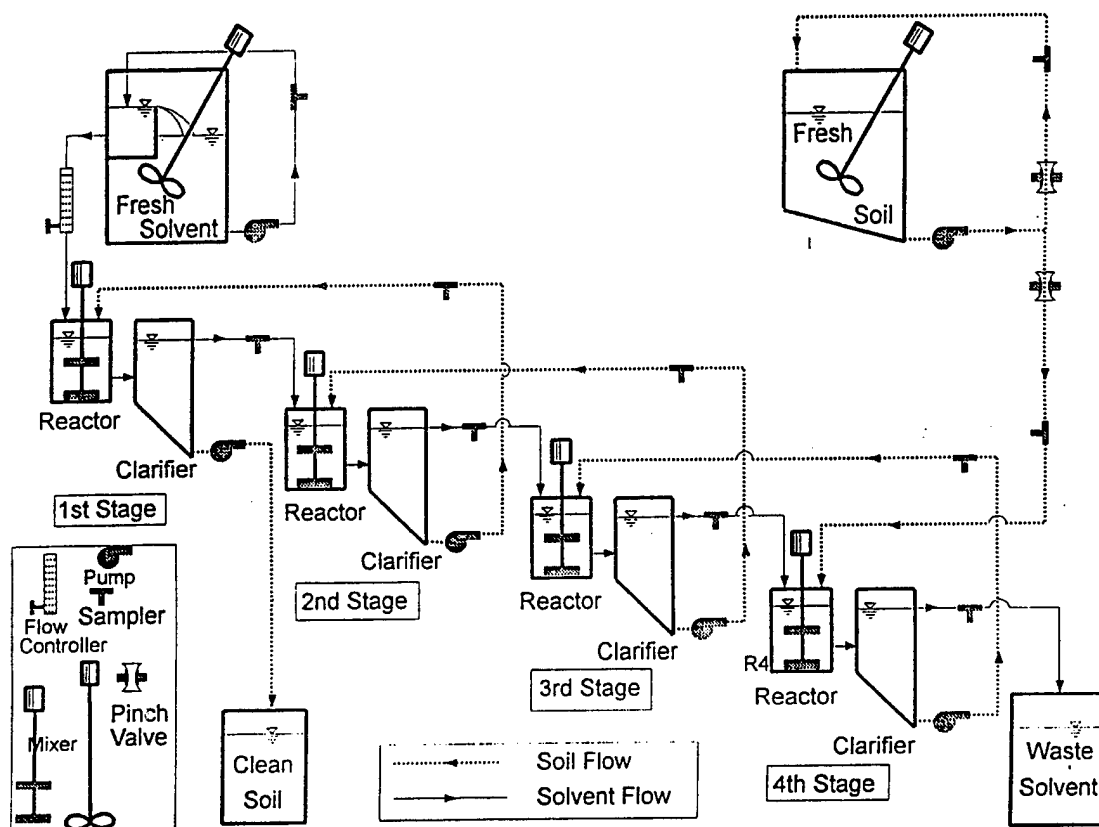
Figure 15. Schematic of the continuous-flow, pilot-scale counter-current metal extraction system.

Operation of Counter-Current Metal Extraction System

One hundred liters of extracting agent were prepared in a 50 gallon Nalgene® tank located adjacent to the first stage reactor and clarifier. The concentrated acid or chelating agent was added to 100 liters of tap water, and the solution was thoroughly mixed using the single speed Lightnin'® Model CS-LB566 mixer. This experimental run was initiated by starting the

extraction solution influent pump at a rate of 277 ml/min. Over the course of approximately one hour, all of the reaction and clarification vessels of Stages 1-4 in the system were filled with fresh extracting agent. For each pilot-scale run, the system was operated for a total of 12 hours.

The feed soil slurry was prepared by slurring 10.8 kg of soil, and 63 liters of tap water were added to a Nalgene® tank to produce a 15percent soil slurry. A Lightnin'® variable speed XJ-30VM mixer was agitated at a speed setting of 5 (~220 rpm) and used to mix the soil and water slurry. Once the reactors and clarifiers were filled with reagent and the slurry was well mixed, all console pump drives (underflow, reagent influent, slurry influent) were set at 100 ml/minute to maximize retention time without causing serious plugging problems in the system. All of the Lightnin'® L1U08F Labmaster variable speed mixers were set at 600 rpm. Total retention time of soil in the counter-current system was approximately three hours.

Samples consisting of 100 ml of slurry and overflow were taken at four, eight, ten, and twelve hours from each of the sampling ports shown in table 10, with the exception of the reagent or solvent sample, which were only collected at the beginning of the test. In an effort to reduce adverse affects on the steady-state flow conditions of the system, samples were collected in a specific order. First, all of the underflow samples (1C, 2C, 3C, 4C) were taken simultaneously and placed in 125 ml Nalgene® HDPE bottles. Afterward, the 4CO sample was collected, followed by the 3CO, 2CO, and 1CO samples (figure 15 and table 10). The final two samples were collected from the fresh soil slurry input (SS) and from the fresh reagent input (Solvent). Console pump flow rates were not adjusted during the sampling period. Each sampling period lasted approximately ten minutes.

Table 10. Counter-current metal extraction system sample identifications.

Sample Identification	Sample Description
1C	1st Stage clarifier solids underflow
1CO	1st Stage clarifier reagent overflow
2C	2nd Stage clarifier solids underflow
2CO	2nd Stage clarifier solids overflow
3C	3rd Stage clarifier solids underflow
3CO	3rd Stage clarifier reagent overflow
4C	4th Stage clarifier solids underflow
4CO	4th Stage clarifier reagent overflow
SS	Initial contaminated solids into system
Solvent*	Initial reagent into system

*Only collected at the start of the test.

After each sampling period, the samples were processed by placing approximately 45 ml of completely mixed sample in the PPCO Oak Ridge® centrifuge tubes. These samples were centrifuged and analyzed as previously described to determine the dissolved metal content. In addition, 20 ml of solids slurry from the clarifier underflow was placed in a 50 ml glass beaker and dried to determine the solids concentration of each of the samples. The solids in the 50 ml beakers were also digested according to EPA Method 3051 (USEPA, 1992) to determine the total metal content in the extracted soil; and the digestions, as well as the liquid samples, were analyzed according to the methods outlined in table 5. The extraction efficiency for each stage and for the overall system was based on the metal content of the influent and effluent solids.

Electrokinetic Evaluations

Soils and Amendments Evaluated

Laboratory EK testing is a very time consuming and expensive process. To minimize the number of experiments that were conducted, the New Orleans soil was not subject to EK testing, and the numbers of duplicated tests were minimized. EK testing for the Ketchikan soil was included because physical and chemical testing could not be conducted on this material due to its unique soil characteristics. No unamended EK tests were conducted because previous research indicates that optimal removal is achieved only when extraction agents are added. The amendments utilized for EK testing were selected based on the results of the batch chemical extraction test. Soils evaluated in the EK test included Cape May, Kodiak, and Ketchikan. Table 11 presents the amendments used in this test.

Table 11. Amendments utilized for the EK laboratory tests.

USCG SAFR Soil	Extraction Agent Utilized	Molar Concentration
Cape May	Nitric Acid: Cathode	0.1
Cape May	Nitric Acid: Cathode	0.1
Cape May	Citric Acid: Cathode	0.25
Cape May	Citric Acid: Cathode/EDTA: Anode	0.25/0.05
Ketchikan	Nitric Acid: Cathode	0.1
Ketchikan	Citric Acid: Cathode/EDTA: Anode	0.25/0.05
Kodiak	Nitric Acid: Cathode	0.1
Kodiak	Citric Acid: Cathode/EDTA: Anode	0.25/0.05

As shown in Table 11, Cape May nitric acid amended cells were replicated. Only four experiments can be operated at any one time, so testing on the Cape May soil was conducted first. Since batch chemical extraction testing was not conducted on the Ketchikan soil selection, the amendments were based on the performance of the amendments for the Cape May soil and previous experience.

Automated System vs Manual System

Electrokinetic soil testing was conducted using two separate laboratory systems. The automated system, which is outfitted with a data acquisition system, automatically recorded and calculated all power and flow readings. The manual system is outfitted to perform the same types of EK evaluations. However, this system does not have a data acquisition system. Data were manually recorded by research technicians for future compilation. The automated system was utilized for the Cape May soil, and the manual system was utilized for the Ketchikan and Kodiak soils. A schematic of the EK testing system is shown in figure 16. Each system was designed in collaboration with Electrokinetics, Inc®. in Baton Rouge, Louisiana for specific use for this project. The systems were designed to produce identical results.
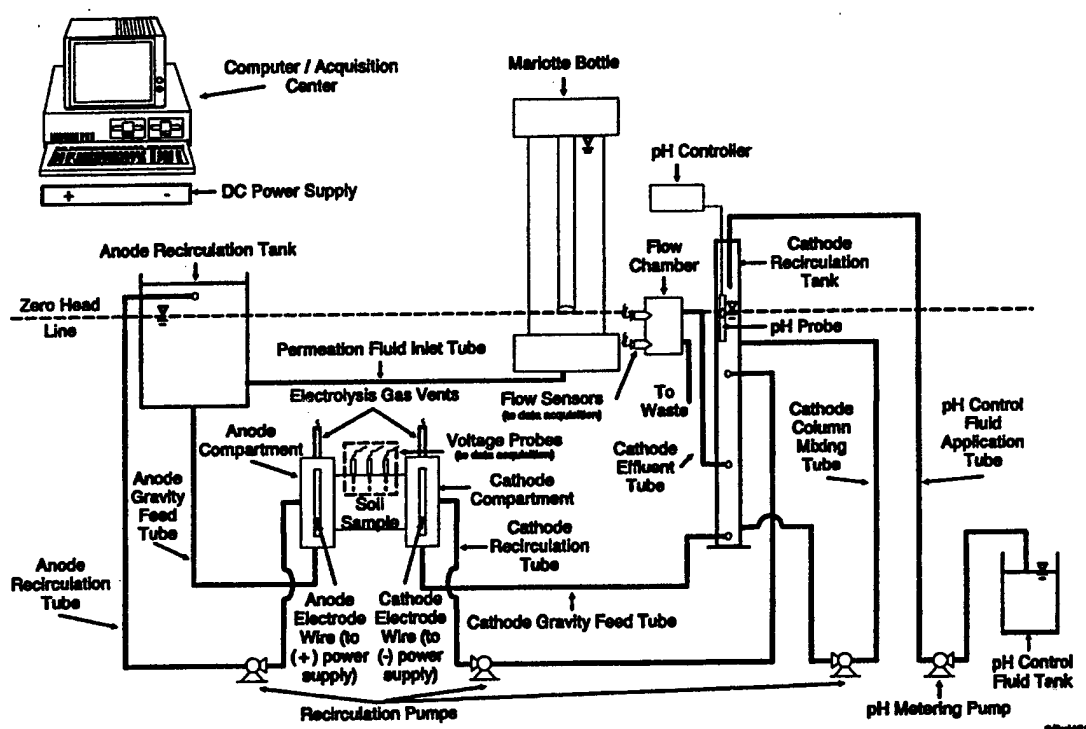
Figure 16. Schematic of electrokinetic remediation system.

Cell Construction and Electrodes

The cells used for both EK systems use the same size of sample and are interchangeable between the two systems, though constructed differently. The cells used in the automated system are basically a redesign of the manual system cells. The new design allowed for easier disassembly of the cells. This proved to be beneficial since it was sometimes necessary to disassemble a cell during a run for such reasons as electrode replacement and precipitation collection. Figure 17 shows a schematic of an EK test cell. The electrodes used in all EK evaluations were Bay Carbon® resin-impregnated carbon electrodes. Carbon electrodes were selected in an attempt to resist electrode degradation since H^+ ions were being created at the anode and low-pH amendments were being added at the cathode.

45
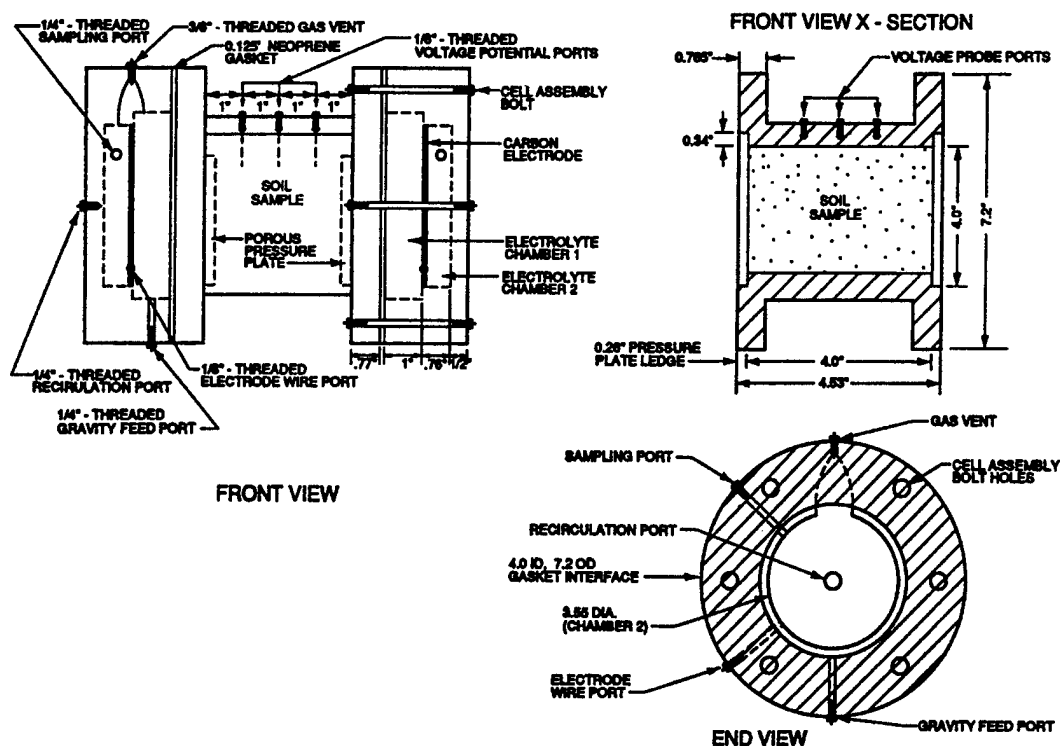
Figure 17. Schematic of electrokinetic test cell.

Cell Flow

Sample flow was recorded in the automated system by flow chambers assigned to each cell. Two optical prism GEM Sensors® were installed in each flow chamber to electronically record flow. Flow from the sample entered at the top of the flow chamber through a ¼-in-nylon fitting. Flow from the KE cell filled the chamber until it contacted the upper sensor. At this point, a Cole Parmer®, Model 01367-71, solenoid valve was tripped in the back of the system, which allowed the chamber to be drained through another ¼-in fitting located at the bottom of the flow chamber. After the chamber was drained, the water level in the chamber was level with the bottom flow sensor, which indicated the calibrated zero point of the particular chamber. Calibrated volumes of each flow chamber were determined; and, by knowing the number of times the chamber was emptied over a known time period, the flow rate was calculated. The manual system was made of a glass drop tube that assisted in measuring the flow rate. The effluent was connected directly to the drop tube, and the waste fluid was collected in a catch basin of known weight. Total flow could then be determined on a weight basis.

Electrolyte Recirculation and Tubing

Recirculation of each electrolyte fluid was done for several reasons: 1) maintenance of zero head across each sample, 2) measurement of electro-osmotic flow, 3) mixing of enhancement/pH control fluid, 4) safe measurement of electrolyte pH, and 5) ease of sampling. The anode and cathode recirculation tanks were constructed out of acrylic and were identical for each system.

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The anode tanks, as shown in figure 16, were constructed with three threaded, ¼-inch ports. The first port, located on the side of the tank, was used for permeation fluid delivery form the Mariotte bottle. The second port, centered on the bottom of the tank, was used as the gravity feed to the anode compartment of the sample. The third port was used for recirculation return of flow from the anode sample compartment.

The cathode recirculation tanks were constructed smaller in order to measure electro-osmotic (EO) flow. Since EO flow could not be predicted and could take place at very low flowrates (< 1 mL/day), it was impossible to measure EO flow with large diameter tanks. Ports were constructed for the same purposes as for the anode tanks. However, two additional ports were constructed for high-rate mixing of the catholyte and pH control fluid.

Masterflex®, Model 7523-30, pumps were used for anode and cathode half-cell recirculation. Masterflex® Tygon® sizes 15 and 16 were used for connection of the anode and cathode gravity feed lines and the recirculation lines, respectively for both systems. Before EK bench scale testing was initiated, the anode and cathode half-cell volumes were determined by filling the cell with water and equilibrating the system to operation head levels. This was necessary because dilution factors were needed for later calculation of metal contaminant concentrations in both half-cell compartments.

pH Control

The pH control/enhancement addition system consisted of NEWPORT® INFC pH controllers and Sensorex® model number SD-200 pH probes for each EK system. The pH control pumps utilized in the automated system were PULSAtron®, Series E-Plus, HANNA® ASP 10 metering pumps were utilized in the manual system. It should be noted that the pH control pumps utilized in the project were very sensitive with regard to pumping rate. After each run, all pumps were cleaned and re-calibrated so that accurate amendment addition could be achieved.

Soil Compaction and Cell Assembly

Normally, soil is compacted into the test cell using a Standard Proctor Compactive Test (ASTM D-698). Soils are compacted just wet of the optimal moisture content using the standard compactive test. The Cape May and Kodiak soils could not be compacted due to the high sand content (and flyash content for the Kodiak soil). The Ketchikan soil also could not be compacted according to the Standard Proctor procedure. Therefore, these soils were processed as follows.

For the Cape May and Kodiak material, wet pre-homogenized soil was transferred directly from the five-gallon sample bucket to the EK test cell with a clean, plastic scoop. Enough soil was placed into the cell in order to fill approximately 1/4 of the middle cell section. The middle cell section was then placed on a vibrating table and vibrated for approximately ten minutes, or until it was visually noticed that no air bubbles were rising to the surface. This procedure was continued until the entire middle cell section was densified. The excess soil was removed, and the surfaces of the cell parts were cleaned. Care was taken that the edges of the soil sample lie flush with the edge of the middle cell section to insure proper fit. A piece of 0.45-μm filter paper was placed on the soil sample interface, and a pressure plate consisting of a pourous

polyethylene disk was placed over the end of the middle cell section to retain the soil and filter paper. Gaskets were inserted into the endpieces containing the outfitted electrodes. The cell was then bolted together. At this point, the cell was now ready for electrical implementation and flow-tube plumbing. Similar procedures were utilized for the Ketchikan soil, except this soil was dampened by spraying water and mixing the soil. This moist soil was compacted into the cell using a plunger that was just slightly smaller in diameter than the cell. Once the cell was filled and relatively free of voids, the cell was assembled as described above.

Final Pre-Test Preparation

The electrode wires were connected to the appropriate negative and positive poles on the DC power supply. The voltage potential wires were placed into the sample and made watertight using small, rubber gaskets. Next, the anode and cathode gravity-feed tubes and re-circulation tubes were connected to the appropriate ports. After all of the electrical wiring and tubing were connected, the entire cell was filled with deionized water (DDI). Proper head levels were then achieved in the anode and cathode re-circulation tanks by directly connecting the Mariotte bottle to each tank and allowing the water level in each tank to equilibrate with the zero-head position in the Mariotte bottle. The pH probes were calibrated using Fisher® 4 and 7 pH buffers and inserted into the cathode column. The system plumbing (re-circulation tubes, gravity feed lines, etc.) was visually checked for air bubbles, since flow would be inhibited with the presence of any large air bubbles. The data acquisition system was turned on during the equilibrium period (for samples run on the automated system only) to allow the water levels to equilibrate with the proper hydraulic head levels in the effluent flow chamber system. All of the pumps were turned on, set to the desired pumping rates, and the system was allowed to equilibrate for two days.

After the system had equilibrated, final test initiation procedures were carried out. The proper enhancement agent/pH control fluid was made and placed into its corresponding holding tank. The data acquisition system was reset, and the power supplies were set to the desired current level, operating under constant current conditions. When the current applied to the cell remains constant, the voltage applied across the cell varies due to the constant change in resistance across the system. A constant current condition was to produce a constant flow of electrons across the system since charge depends on current, not voltage, in an electrolytic cell.

The pH control fluids were automatically pumped into the cathode columns by the pH control metering pumps assigned to each EK cell. The pH controllers allowed for a set point to be entered which tripped a relay in the controller whenever the set point was exceeded by 0.1 pH units. Whenever the relay was tripped, enough pH control fluid was pumped into the cathode column to lower the pH below the set point. The set point used in all EK tests was the pH value of 3. Therefore, when the pH of the cathode columns exceeded 3.1, pH control fluid was added until the pH of the half cell was lowered below 3. The metering pumps were automatically shut off once the pH of the half cell was lowered just below (0.05 sensitivity) a value of 3.

EK Cell On-Line Sampling

Day-to-day sampling and maintenance were conducted on each system during every EK test. The systems were checked for leaks daily. However, samples and readings were taken every other

day (the automated system took readings automatically every hour). Anolyte and catholyte samples were taken in an attempt to obtain electrolyte concentration removal rates over time. Voltage readings were taken so that power and cost requirements could be estimated for each soil. Flow readings were recorded so that corrected EO flow rates could be calculated. EO flow was determined by the equation shown below.

$$Flow_{EO} = Flow_{total} - Control\ Fluid\ Volume \qquad (3)$$

where:

$Flow_{EO}$ = the volume (mL) of permeation fluid transported through the system as a result of the applied electrical field.

$Flow_{total}$ = the total volume (mL) of fluid.

$Control\ Fluid\ Volume$ = the volume (mL) of pH control fluid that was added to the system to counteract the OH⁻ ion production at the cathode.

Total flow was recorded by reading the effluent value directly from the graduated cylinder assigned for effluent collection. The pH control fluid tank (graduated cylinder) was filled to the 1000 mL mark at the beginning of the test. The amount of pH control fluid utilized between sample days was simply read directly from the control fluid tank. After taking the appropriate readings, the cylinder was refilled to the 1000 mL mark.

Anolyte and catholyte samples were taken from ports located on the half-cell sections of the cell. Approximately 50 mL of sample were taken from each half-cell compartment. The anode fluid was automatically replaced by the Mariotte bottle that was always connected to the anode recirculation tank, while the cathode fluid was manually replaced with 50 mL of DDI that was poured directly into the cathode re-circulation tank. Replacement of these fluids was necessary to maintain zero hydraulic head difference across the system so that correct electro-osmotic flow values could be determined.

Post-Run Cell Disassembly and Analysis

After completion of each test, the power supplies were turned off, and the electrode wires were disconnected. The cell was disassembled, and notes were taken to outline such information as precipitation formed, post-run electrode color, filter degradation, etc. The post-run EK soil samples were sliced into four, 2-1/2 cm sections with a stainless steel knife. The knife was washed with DDI and wiped with a Chemwipe® before cutting different sections. Each sub-section was weighed and stored in Ziplock® disposable bags at 4°C awaiting further analysis.

Each sub-section was homogenized thoroughly and prepared for final analysis. Approximately 40 to 50 grams of soil taken from each sub-section were weighed for moisture analysis and metals analysis. Sub-section pH was also determined, and the soils were digested and analyzed for metals content. All sub-section results were averaged in order to obtain a four-section profile across the cell with regard to pH, moisture content, and metal contamination. It should be noted that system preparation (re-calibration, rewiring, making of solutions, housecleaning, etc.) took approximately one week, while post-run tasks usually lasted anywhere from three to four weeks. Therefore, depending on the length of a test, completion of an entire series took at least four months from start to finish.

Results

Results of the Core Samples and Surface Samples

Training Center Cape May

A total of 42 core samples were collected from the SAFR berm and surrounding area at the Cape May facility. Detailed results of the metal analysis were provided to the USCG. While this sampling effort focussed primarily on the soil contained in the old impact berm, samples were also collected in an area to the Northwest, the Southwest, and the Southeast. The impact berm at Cape May has a steep slope. While grass covered the right side of the berm, the left side appeared to have sluffed and was undergoing some effects of erosion. It is expected, based on the berm's appearance, that the right side of the berm would be less contaminated than the left side due to soil movement.

Cape May personnel indicated that maintenance had recently been conducted on the berm and that fresh, clean sand had been placed on the surface of the berm. The sampling results reflect this. Typically, near the top of the berm high levels of lead are not observed at the surface of the soil. However, a substantial amount of lead was found below the soil depth of approximately 9 inches. At the toe of the berm, elevated lead levels were found at the surface and up to the maximum sampling depth of 40 inches. Accumulation of lead at the toe of the berm may have resulted from the downward migration of lead and contaminated soil.

The core sampling data are also highly variable. Typically, data from other SAFRs indicate that as depth increases, contamination levels decrease. While some general trends are exhibited by the data (as discussed in the previous paragraphs), there is a high degree of scatter. This data scatter may reflect soil mixing which resulted during the berm maintenance activities or contaminant dissolution and vertical migration. The core sampling results indicate that lead levels in excess of 400 mg/kg (a typical action level) are measured in at least one section of almost every sample collected. In some cases, the lead levels are in excess of 10,000 mg/kg. In contrast, copper levels are relatively low. Only sporadic elevated levels of copper were detected (> 400 mg/kg). Normally, this is observed when the soil lead concentrations are elevated. Antimony is the only other metal that was analyzed that was consistently detected above the detection limit.

While the exact age of the SAFR is not known, it is suspected that the berm was used for 20 to 30 years. When the berm at Cape May was compared to similar ranges, significantly fewer bullets and bullet fragments were observed in the Cape May soil. Of the bullet fragments that were observed, most were severely weathered. Previous studies (Bricka et al., 1999 and Bricka, 1998) indicate that elevated salt conditions accelerate corrosion of bullets. Because the range is located very close to the ocean and elevated lead levels were observed in the berm's soil, it is suspected that the ocean spray is accelerating bullet dissolution.

Integrated Support Command Ketchikan

Core Samples

A total of 55 core and surface samples were collected from the Ketchikan SAFR. A detailed report of the Ketchikan sampling activity was presented to the USCG under separate cover (Teeter et al., 1999a). Analysis indicated that most core and surface samples had lead concentrations greater than or equal to background concentrations (254 mg/kg lead). At most sample locations, lead contamination of the core samples decreased with depth. Lead concentrations reached or approached background concentrations at the soil depth of 15 inches. Elevated lead concentrations were found at depths greater than 15 inches at five locations.

Elevated levels of copper were also noted at Ketchikan as compared to other SAFRs investigated by the WES. As stated previously, most military projectiles are copper jacketed and as the projectile enters the soil, the jacket is fractured. The elevated copper levels in the soil may be attributed to the copper jacket separating from the lead core or to the dissolution of the copper by the acidic soil.

TCLP Results

The TCLP analysis was conducted on selected Ketchikan soil samples. Samples were chosen for analysis based on high lead concentrations and to obtain a representative sampling over the Ketchikan SAFR. According to the TCLP criteria, lead is the only regulated constituent. Other contaminants analyzed for during the TCLP methods were Cr, Cu, Sb, and Zn. Soil samples with leachate lead concentrations above 5 mg/l failed the TCLP protocol and are subject to regulations for a hazardous waste material. Using 5 mg/l as a lead concentration in soils, all but four samples failed the TCLP test.

Integrated Support Command Kodiak

Core Samples

To achieve a high degree of accuracy and to adequately represent the sample area at the Kodiak SAFR, 55 core and surface samples were collected. Surface samples were collected to approximately four inches, and core samples were taken to maximum depths of approximately three feet. A more detailed report of this sampling activity was presented to the USCG under separate cover (Teeter et al., 1999b). Soil samples which are at levels of concern, based on previous studies (Bricka, 1996a and 1996b), are those with greater than 100 mg/kg lead. Results of the surface samples collected showed that eleven of the nineteen samples analyzed had lead concentrations greater than 100 mg/kg. Based on studies of SAFRs, (Bricka ,1996a and 1996b), it is not uncommon for high levels of lead to be found at SAFRs. This is generally the area where there are a large number of expended munitions. The highest concentration of lead was found at the surface of the soil. Elevated soil lead concentrations were measured in all core sections from the surface (0 inches) to 26.5 inches at many of the sample locations. In general, the concentration of lead typically decreases with depth; however, considerably higher concentrations of lead were found deeper in the soil in several of the samples. It is possible that a bullet fragment was present in these core sections.

TCLP Results

The TCLP analysis was conducted on selected Kodiak soil samples. According to the TCLP criteria, lead is the only regulated constituent. Other contaminants analyzed during TCLP included Cr, Cu, Sb, and Zn. Soil samples with leachate Pb concentrations above 5 mg/l fail the TCLP protocol. These include soil samples primarily located in the berm area where the highest concentrations of metals were found. These samples may be considered hazardous and require some form of special handling.

Communications Station New Orleans

Soil Pile

Fifteen core samples were collected from the soil pile at the New Orleans SAFR. This area contained a mound of soil that range personnel indicated had been excavated from the SAFR berm after problems were encountered with ricochets. New sand had been placed on the berm, and the excavated soil had been deposited nearby. The soil pile had several young trees growing in the soil as well as a grass cover, and appeared to have been deposited at this location for two to three years. Because this soil was removed after years of use as an impact berm material, it was expected that the lead concentration of the soil would be high. Initial observation of the soil pile revealed that numerous bullet projectiles could be identified just under the vegetative cover. These consisted of intact bullets and bullet fragments. The metals analysis indicated that a significant number of the core samples had high levels of lead (> 400 mg/kg) while the other metals were relatively low. The samples with high lead concentrations generally had elevated lead to a depth of approximately twenty inches. Four samples collected in the soil pile had relatively low lead levels. It appears more contamination can be attributed to the Northwest end of the soil pile than to the Northeast end of the soil pile. This may have resulted from how the soil was placed in the pile. If contaminant migration is occurring from the soil pile, it appears limited to the area near the waste pile and is isolated in the surface of the soil. Initial estimates indicate that the soil pile consists of approximately 300 cubic yards of soil.

Small Arms Range Berm Sampling

Samples were also collected from the active berm at the New Orleans SAFR, as well as the soil between the firing line and target line. Six core samples were collected from the berm, and another six core samples were collected from the area in front of the berm. Samples that were taken from an area approximately 56 feet from the firing line were relatively free of metal contaminants. However, the other samples all had significant lead concentrations. Most of the samples collected from the berm had lead contamination in the surface (3 to 6 inches), an area of relatively clean soil (6 to 30 inches), and a deeper area of high contamination (> 30 inches). It was also observed that the samples located higher on the berm were less contaminated than the samples taken at locations lower on the berm.

It is suspected that these data trends result from the soil excavation and the reuse of the range. If soil deeper in the berm was not removed and a fresh layer of sand was placed over the soil, it

could account for the deeper contamination covered by a clean soil layer. Surface contamination of the fresh soil may have resulted from the relatively short period of range reuse since refurbishment. The rounds expended into the berm after the soil was removed may not have migrated very deep into the soil, except in the area of intense use (lower on the berm). The area close to the target line could have been contaminated by soil washing down the face of the berm and depositing in the area near the wall supporting the berm.

Field moisture and pH were also analyzed for selected samples at this site. These data indicate that the soil pH for the site is relatively low and that the moisture of the soil is high. Low soil pH could account for the deeper contamination measured in some samples.

Untreated Soil Characterization

Bulk Chemical Analysis

Bulk samples were collected from the four sites. Results of the averaged metal analysis are provided in table 12. Ten bulk samples were collected at two sites (five from each site) from the impact berm at Cape May. After the analysis confirmed that these samples had similar concentrations of contaminants, these samples were combined and homogenized to produce the Cape May bulk sample.

Table 12. Average bulk soil concentration.

Soil Site	Cd	Cr	Pb	Zn	Cu
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cape May	8	<DL	1050	50	82
Ketchikan	11	<DL	23200	325	1420
Kodiak	51	17	15000	32	580
New Orleans	<DL	<DL	1390	41	88

Seven bulk samples were collected from the Ketchikan SAFR. While the contaminant analysis of these soils varied, drying of this sample substantially reduced its weight. All seven bulk samples were combined and homogenized to produce the Ketchikan bulk sample.

Eight bulk samples were collected at two sites (four from each site) from the Kodiak impact berm. After the analysis confirmed that these samples had similar concentrations of contaminants, these samples were combined and homogenized to produce the bulk sample.

At the New Orleans site, bulk samples were collected from the soil pile and the impact berm. Eight bulk samples were collected from a single site on the soil pile. Four bulk samples were collected from a single site on the impact berm. Analysis of these bulk soils indicated that higher concentrations of metal contaminants were measured in the bulk sample collected from the soil pile. Thus, the eight samples from the soil pile were combined and homogenized, and the four

samples from the impact berm were homogenized; but these samples were kept separate from the soil pile bulk sample. Due to the higher concentration of contaminant contained in the New Orleans soil pile material, this sample was utilized for the majority of the laboratory experiments.

The results presented in table 12 indicate that there is very little Cd or Cr contamination in the four soils. The Kodiak soil has the most contamination. As expected, Pb is the contaminant with the highest concentration for all the soils.

TCLP

TCLP testing was performed on the four bulk samples. The average TCLP results for bulk soils are presented in table 13. These results indicate that lead is greater than 5.0 ppm for all the bulk soils. Leaching of the other contaminants is low although these contaminants are not regulated under the TCLP.

Table 13. Average TCLP soil concentration.

Soil Site	Cd mg/kg	Cr mg/kg	Pb mg/kg	Zn mg/kg	Cu mg/kg
Cape May	<DL	<DL	16	7.3	3.7
Ketchikan	0.07	<DL	368	0.6	0.5
Kodiak	0.1	<DL	26	1.3	3
New Orleans	<DL	<DL	39	0.9	4

Particle Density

The particle density of the four bulk soils was determined. The results of these tests are presented in table 14. These results indicate that the particle density of Ketchikan soil is much lower than the other soils. The average particle density of soil is reported to be 2.65 g/cc (Perry and Green, 1984). The Cape May, Kodiak, and New Orleans soils have particle density close to the reported value. This particle density provided numerical data that the Ketchikan soil is very different from the other three soils.

Table 14. Average particle density.

Soil Site	Density (g/cc)
Cape May	2.7215
Ketchikan	1.6191
Kodiak	2.581
New Orleans	2.6417

Buffering Capacity

The results of the buffering capacity test are presented in figure 18 for the New Orleans and Ketchikan bulk soils. The data in this figure indicate that to lower the pH of the soil to 4.0, approximately 0.25 millimoles of acid must be added for each gram of New Orleans soil, but only 0.005 millimoles of acid are required for Ketchikan. The buffering capacities of other military SAFRs' soils are presented for comparison purposes. This data provides an indication that the Ketchikan soil has very little acid neutralization capacity, thus this soil is acetic and may be treated effectively with metal extraction processes. In contrast, the New Orleans soil has a strong buffering capacity. It is likely that chemical extraction processes may be ineffective forms of treatment.
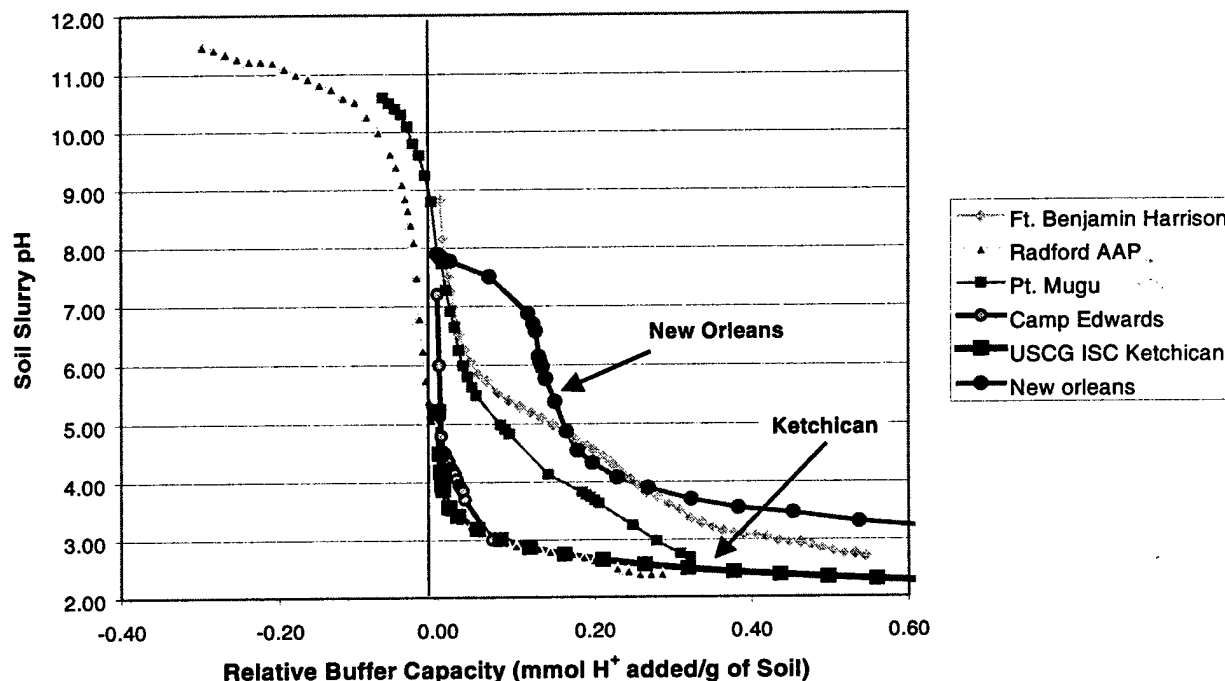

Figure 18. Comparison of the buffering capacity of New Orleans and Ketchikan soils to other military soils.

Physical Separation Studies

Particle Size Assay

Training Center Cape May

Non-attrited Particle Size Assay

The bulk sample collected from the impact berm was subjected to the particle size assay (PSA). While soils subjected to PSA were extracted and analyzed for all contaminants of concern (COC), only lead was measured at levels that warrant additional discussion. Very little weight of the Cape May bulk soil is attributed to the greater than 6.0 mm soil size fraction. This indicates that very few large rocks or large debris are found in this soil. This was expected because the Cape May soil is composed mostly of beach sand. A large portion of the lead (70%) is contained in the 6.0-2.0 mm particle size fraction, while only a small percentage of the soil mass (4.5%) is included in this size fraction. The bulk of the remaining lead (11.5%) is contained in the < 0.063 particle size fraction. Although very little lead mass is attributed to the remaining particle size fractions, the larger particle fractions (2.0-1.0 and 1.0-0.5) have a substantial quantity of TCLP extractable lead. It appears from this data that only the 0.5-0.25, 0.25-0.125, and 0.125-0.063 size fractions would be amenable to particle size separation. These fractions account for over 75% of the soil mass, thus a substantial reduction in the volume of the soil requiring additional handling would result if the soil could be backfilled without additional treatment. Unfortunately, all three of these fractions have TCLP values in excess of 5 mg/l.

Because the bulk soil was collected from the top twelve inches of the soil surface and, as explained earlier, the upper layer of soil on the berm is relatively free of contamination, the bulk lead concentration is reported to be 940 mg/kg. This contaminant concentration is likely to be lower than what would be observed during an actual berm excavation. If this is true, it is unlikely that the soil from the 0.5-0.25, 0.25-0.125, and 0.125-0.063 size fractions will pass the TCLP when remediation activities are commenced because of the increased contaminant content of these fractions.

Attrited Particle Size Assay

Attrition results for bulk Cape May soil show a slight shift in soil mass distribution towards the finer particle size for the for the attrited soil compared to the non-attrited soil. The concentration of lead in the < 0.063 particle size fraction was substantially increased. This is a result of freeing small agglomerated soil particles that contain high levels of lead. While attrition was successful in shifting the lead concentration to the < 0.063 size fraction and resulted in lowering the concentration of lead for most size fractions, only the 0.25-0.125 size fraction passed the TCLP.

Although only one soil fraction passed the TCLP, the fact that the 0.25-0.125 size accounted for over 35% of the soil mass is significant. A 35% reduction of soil mass requiring treatment could result in a significant reduction in treatment costs. While many factors could influence the economics and successful application of attrition scrubbing, the use of attrition scrubbing in a full-scale treatment scenario should merit additional consideration based on these results.

Integrated Support Command Kodiak

Non-attrited Particle Size Assay

The bulk sample collected from the impact berm at the Kodiak range was subjected to the PSA. While soils subjected to PSA were extracted and analyzed for all COC, the Cu and Zn exhibited trends that were reflected in the Pb data. Thus, this discussion focuses primarily on the Pb contaminant. Very little weight of the Kodiak bulk soil is attributed to the greater than 6.0 mm soil size fraction, indicating very few large rocks or large debris are found in this soil. This was expected because the Kodiak soil is composed mostly of a fine flyash and sandy material.

A large portion of the lead (64%) is contained in the 6.0-2.0 mm particle size fraction and the < 0.063 fraction. Unfortunately, a large portion of the soil mass contributes to these fractions (56%). The remaining five middle fractions contain metal concentrations which are relatively equally distributed among them. Each fraction contains TCLP leachable lead. The bulk sample contains high concentrations of lead, and excavated soils are expected to have lower concentrations of lead than that found in this sample due to the mixing action of the excavation process. Even if the soil has lower lead concentrations, it appears that only the 0.25-0.125 and 0.125-0.063 size fractions have the possibility of having lead contaminant levels low enough to merit backfilling of the soil onsite without additional treatment. These two fractions account for only 12% of the soil's weight. Based on these results, the use of particle size separation technologies does not appear to offer a large benefit for the treatment of Kodiak SAFR soils.

Attrited Particle Size Assay

Attrition particle size assay analysis was not conducted on the Kodiak SAFR soil. The limited volume of soil collected did not permit the investigation of attrition testing. Based on the results of the non-attrition PSA studies, attrition scrubbing is not expected to be highly effective for the Kodiak soil.

Communications Station New Orleans

Non-attrited Particle Size Assay

The bulk sample collected from the soil pile at the New Orleans SAFR was subjected to the PSA. While soils subjected to PSA were extracted and analyzed for all COC, only lead was measured at levels that warrant additional discussion. Results showed that physical separation of the unattrited soil is ineffective in concentrating the lead contaminants. The soil is poorly graded, with most of the soil's weight concentrated in the <0.5 mm and smaller fractions. Of these smaller fractions, those having higher soil mass also have higher lead concentrations. While the 0.125-0.063 size fraction passes the TCLP criteria of 5 mg/l, this only accounts for 5.7% of the soil mass. Based on these results, the use of particle size separation technologies does not appear to offer a large benefit for the treatment of New Orleans SAFR soils collected from the soil pile.

Attrited Particle Size Assay

The attrition PSA was not conducted on the New Orleans soil pile soil. Based on the result of the non-attrition PSA studies, attrition scrubbing is not expected to be highly effective for this material and thus was not conducted.

Wet shaker Tabling Analysis

Training Center Cape May

Non-Attrited Tabling Results

The results of the non-attrition wet shaker tabling for the Cape May soil appear very promising. These results indicate that the largest amount of soil reports to the mids fraction (approximately 75%). The remainder of the soil is distributed between the cons and the tails. While the total Pb contained by the mids fraction is large (49%), the concentration of the lead in this fraction is low (99 mg/kg). The TCLP results also indicate that the lead remaining in the soil is not highly mobile as measured by the TCLP, only leaching 1.5 mg/l. In contrast, the tails fraction accounted for only 1.0% of the soils weight but contained over 24% of the lead mass, resulting in a total lead concentration of the tails of greater than 3600 mg/kg.

Attrited Tabling Results

Attrition appears to have a beneficial effect only on the tabled lead contaminant when compared to the non-attrited lead results. The most significant effect of attrition is that soil mass of the mids fraction increases from 75% to over 89% while the total lead concentration decreases from 99 to 57 mg/kg. The TCLP extract concentration increases slightly (from 1.5 to 3.1), although it is expected that this would decrease due to the decrease in lead concentration. This increase in TCLP extract concentration is attributed either to a particle of lead contained in the soil sample subjected to the TCLP or to the inherent variability of the TCLP test.

Integrated Support Command Kodiak

Non-Attrited Tabling Results

The results indicate that tabling of the SAFR soil from Kodiak is not very effective in concentrating the lead in a small soil mass. Although tabling effectively separated the soil into the three fractions, when the soil mass fraction is high, the lead concentration of the fraction is also high. While the concentration of Pb is very high for the bulk Kodiak soil (over 19,800 mg/kg), under actual excavation conditions it is expected to be much less. It is suspected that tabling will be even less effective for the less contaminated Kodiak soil.

Attrited Tabling Results

As in the PSA test, attrition of the soil for the tabling study was not conducted due to the limited volume of soil collected from the Kodiak SAFR. However, based on the result of the non-attrition tabling studies, attrition scrubbing is not expected to be highly effective for this soil.

Communications Station New Orleans

Non-Attrited Tabling Results

The results for the Pb contaminant at the New Orleans SAFR indicate that tabling of the non-attrited SAFR soil from New Orleans is not highly effective in concentrating the lead in a small soil mass. As observed with the Kodiak tabling results, when the soil mass fraction is high, the lead concentration of the fraction is also high. Approximately equal quantities of soil are distributed in the mids and cons fractions (48 and 40%, respectively). The mids and tails fractions pass the TCLP of level 5 mg/l, which is very positive, but the soil Pb concentration of the tails fraction is quite high (> 1000 mg/kg) which may require additional treatment for this fraction prior to disposal.

Attrited Tabling Results

The attrition results for the New Orleans SAFR soil appear to be an improvement over the non-attrited soil. Attrition increases the mass fraction of the mids from 48% to over 67%. This is a substantial increase in the mids mass. Also, it is observed that the concentration of Pb in this fraction drops from 290 to 241 mg/kg. Only 1.1 mg/l of lead was leached from the attrited mids fraction in the TCLP test. The remaining fractions (cons and tails) account for just over 32% of the soil mass but contain over 65% of the total weight of the Pb. Based on these results, attrition tabling of soil from the New Orleans soil pile may warrant further consideration as a potential remediation technique.

Summary of the Physical Separation Tests

Results of the physical separation tests indicate that of the three USCG range soils examined as part of this study, particle size separation and tabling is most effective for the Cape May soil. Attrition appears to increase the effectiveness of these treatments for the Cape May soil. Tabling coupled with attrition scrubbing appears to be moderately effective for the New Orleans soil pile material. In contrast, physical separation technologies are ineffective for the Kodiak SAFR soil.

Soil Chemical Extraction Evaluations

Batch Chemical Extraction Results

Training Center Cape May

Batch extraction tests were performed on the bulk soil collected from the impact berm at Cape May. The removal efficiency of each of the reagents was based on the following equations. Equation (4) is used to determine the milligrams of dissolved metal in the extract per kilogram of soil used in the batch test.

$$Q_1 = \frac{C_d * V * (UC_1)}{W} \tag{4}$$

Where:

Q_1 = metal extract (*mg* metal/*g* soil)
C_d = dissolved metal in liquid (mg/*L*)
V = sample volume (*ml*)
W = sample weight (*g*)
UC_1 = volume unit conversion (1 L/1000 *ml*)

Equation (5) yields the *mg* of total metal per kilogram of bulk soil used in the batch test.

$$Q_2 = C * UC_2 \qquad (5)$$

Where:

Q_2 = total metal (*mg* metal/*g* soil)
C = total metal in untested soil (*mg/kg*)
UC_2 = weight unit conversion (1 *kg*/1000 *g*)

Equation (6) calculates the percent metal removal by comparing the values found in Equations (4) and (5).

$$R_1 = \frac{Q_1}{Q_2} * 100 \qquad (6)$$

Where:

R_1 = percent metal extracted from soil (*%*)

Using Equations (4), (5), and (6), percent removal efficiencies were calculated for each of the reagents used in the batch study. Figure 19 presents the results of the lead batch extraction studies for the Cape May soil. This test only serves to assist in identifying the extraction agents which have the potential to treat the soil. Lead is the only contaminant presented because, for chemical extraction treatment to be successful, the lead concentration of the soil must be reduced. The results presented in figure 19 indicate that three acids (nitric (HNO_3), hydrochloric (HCl), and citric) as well as three chelating agents (EDTA, NTA, and DTPA) were effective in extracting over 50% of the lead contained in the Cape May soil. HCl appears to be the most effective extractant evaluated for the Cape May soil. HCl extracted over 73% of the lead at a 0.01M. Close examination of the HCl data also indicates that at the higher HCl concentration (0.05M and 0.1M), the extraction efficiency actually decreased. This was unexpected. HNO_3, in contrast, exhibited extraction efficiencies almost as high as HCl. At the highest concentration evaluated (0.1M) HNO_3 removed over 67% of the lead; and at the 0.05M concentration, HNO_3 achieved a 61% removal.

The chelating agents were almost as effective as the acids. On average, EDTA removed approximately 60% of the lead; NTA removed 58%; and DPTA removed 56%. Based on the results of the batch extraction test, it is believed that the general category of strong acids and chelating agents provide the best extractants. To insure representation of these categories of extracts in the counter current extraction test, it was decided that EDTA at a 0.5M concentration and HNO_3 at a 0.5M concentration should be evaluated in the counter-current metal extraction (CCME) pilot studies portion of this study for the Cape May soil.
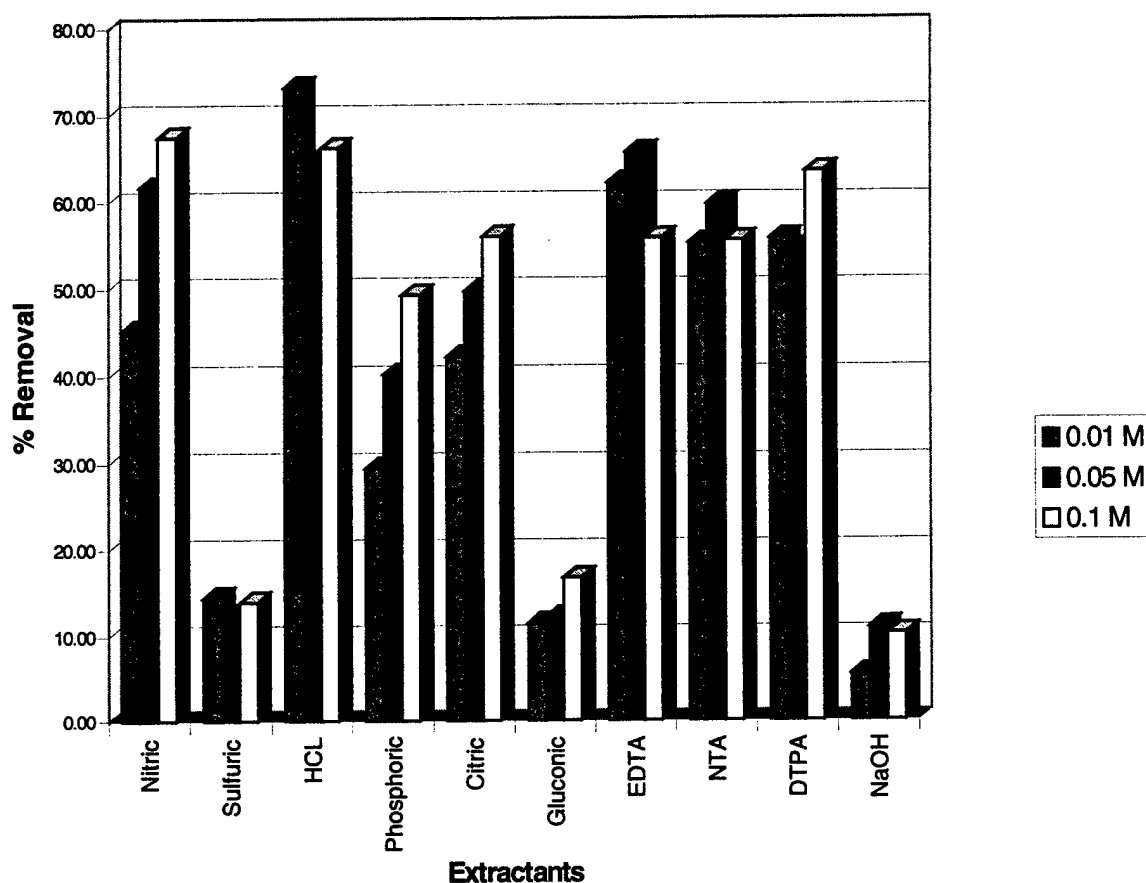
Figure 19. Lead results for the batch extraction of the Cape May SAFR soil.

Integrated Support Command Kodiak

Results of the batch chemical extractions of the lead contaminant for the soil collected from the impact berm at the Kodiak SAFR are presented in figure 20. As observed in the Cape May soil batch extraction, the three acids (nitric, hydrochloric, and citric) and the chelating agents (EDTA, NTA, and DTPA) were effective in extracting almost 100% of the lead contained in the ISC Kodiak soil. It should be noted that the 0.01M and 0.1M DTPA are missing due to sample loss that occurred during testing. Such high extraction efficiencies were unexpected when compared to the Cape May results because the concentration of the lead contained in the Kodiak soil (20,000 mg/kg) was much higher than the Cape May soil (800 mg/kg).

For the Kodiak soil, HNO_3 at the 0.05M concentration was selected for evaluation in the CCME pilot studies. Citric acid at the 0.05M concentration was also evaluated in the CCME pilot studies, due to the effectiveness of the citric acid in extracting lead from the Kodiak soil and because it is a weak acid. While EDTA and the other chelating agents were just as or more effective, the use of citric acid would allow another category of extracts (weak acids) to be examined as part of this study.
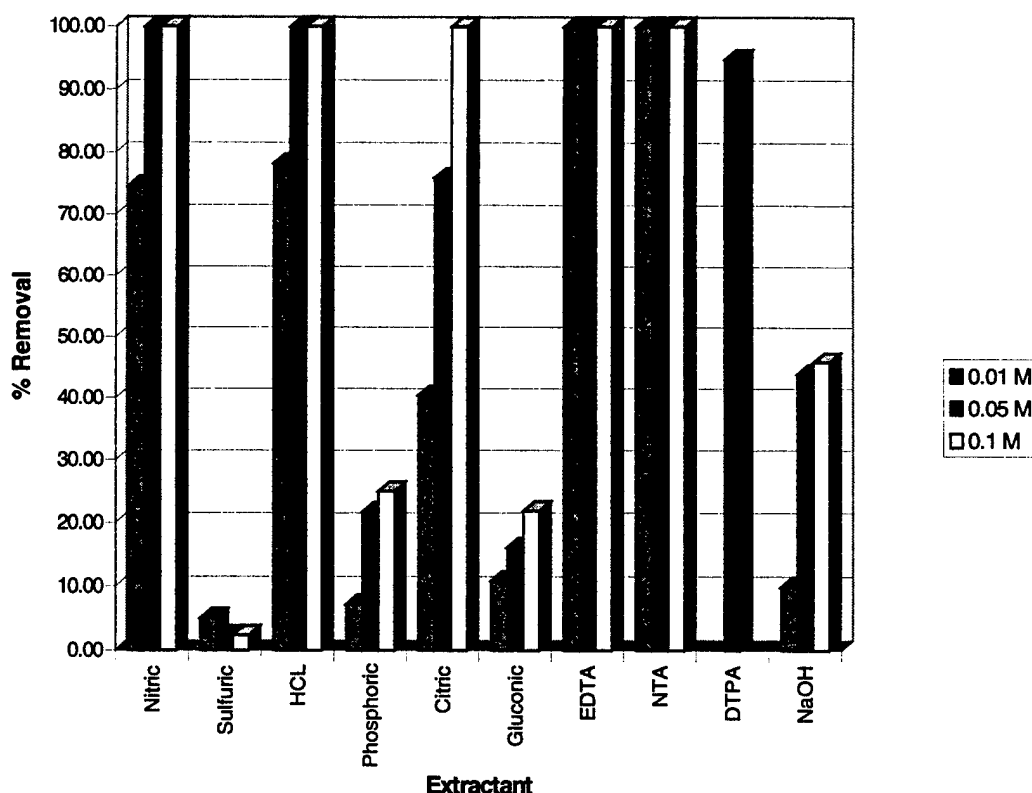
Figure 20. Lead results for the batch extraction of the Kodiak SAFR soil.

Integrated Support Command New Orleans

Results of the batch chemical extraction of the lead contaminant for the soil collected from the impact berm and the waste soil pile located at the SAFR at New Orleans are presented in figures 21 and 22. When compared to the Cape May and Kodiak results, it is evident that the lead contained in the New Orleans soil is much less amenable to chemical extraction.

The New Orleans soil collected from the soil pile on average had 20-30% of lead contaminant extracted in the batch test (figure 21). While the bulk concentration of the waste pile material was relatively high (approximately 1000 mg/kg), the concentration of the bulk soil collected from the impact berm was much lower (100-150 mg/kg). Results of the batch chemical extraction for the impact berm soil appeared to be more effective with extraction efficiencies as high as 80-100% (figure 22). When the contaminant level is considered, the quantity of lead extracted from the impact berm material is much less than that extracted from the soil pile material. Chemical extraction for both New Orleans soils does not appear to be highly effective.

The New Orleans "soil pile" bulk soil was tested in the pilot CCME system; however, the bulk New Orleans "impact berm" soil was not evaluated. The soil pile was selected for additional study because remediation of this soil may be required before the impact berm, also that the concentration of the lead contained in the impact berm bulk soil was relatively low. Based on the results shown in Figure 24 and the extractants selected for pilot CCME testing for the Cape May and Kodiak soils, HNO_3 and EDTA were selected for pilot CCME investigation of the New Orleans soil pile bulk soil.
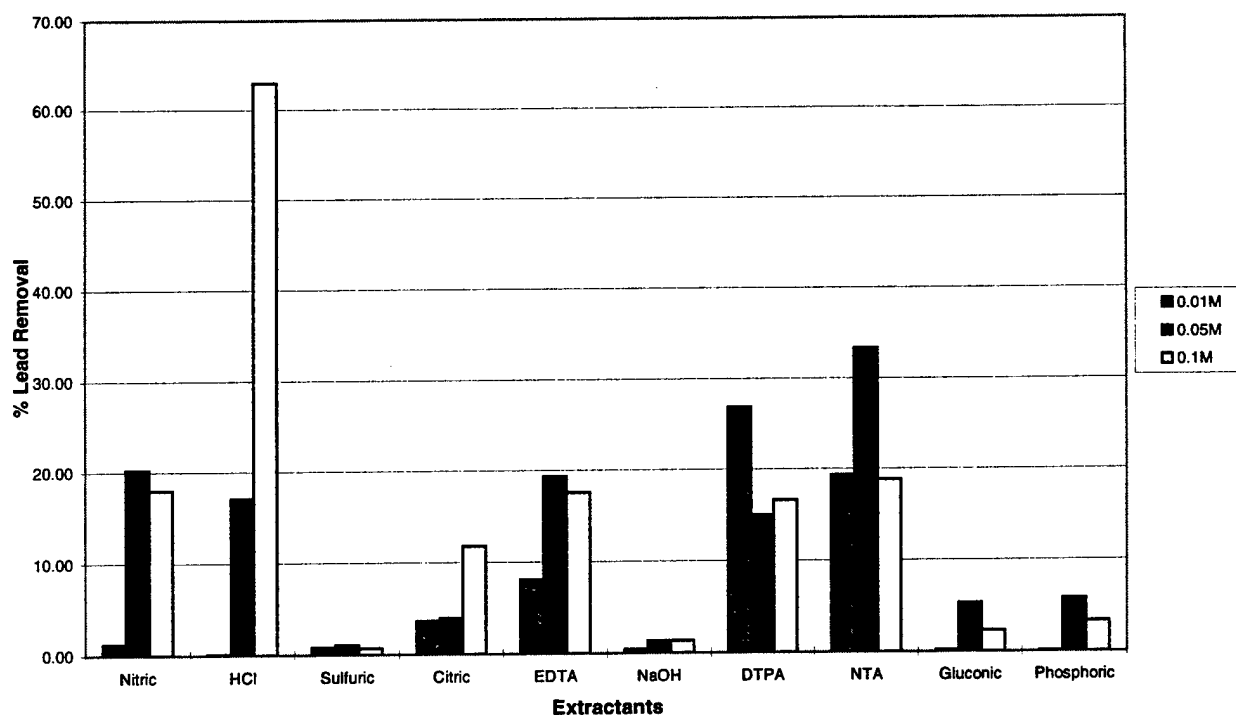
Figure 21. Lead results for the batch extraction of the New Orleans soil pile SAFR soil.
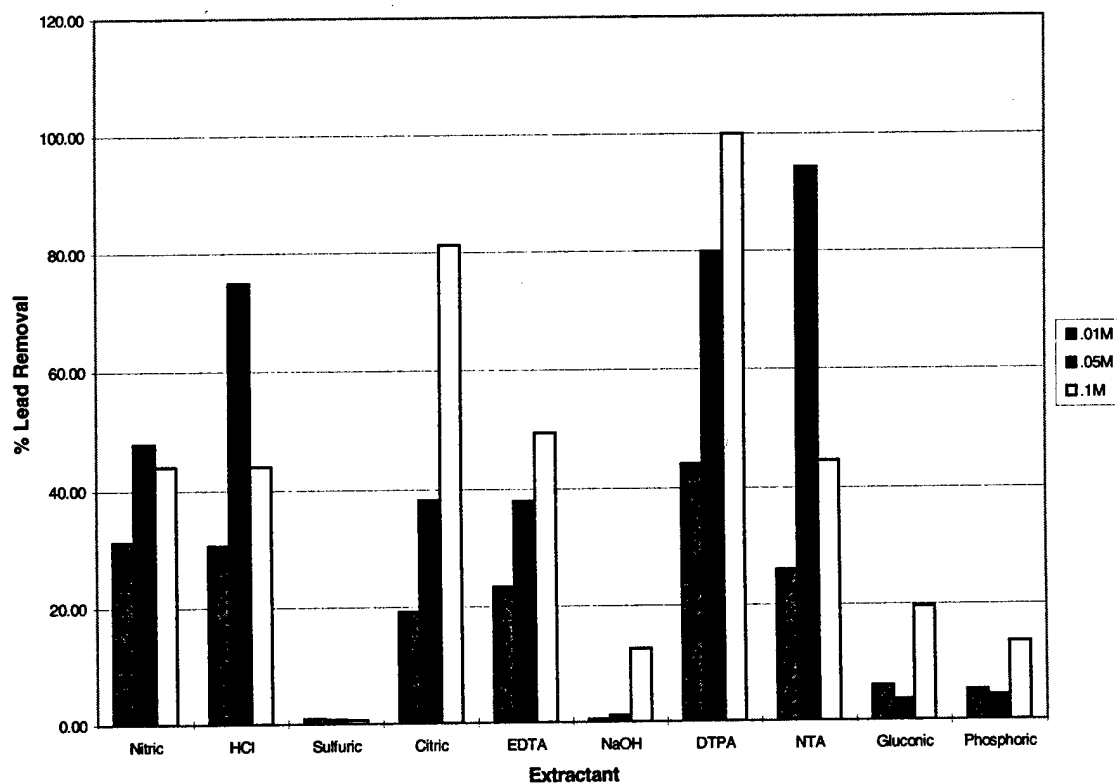

Figure 22. Lead results for the batch extraction of the New Orleans impact berm SAFR soil.

Counter-Current Metal Extraction System Results

The objective of the CCME pilot tests was to determine the feasibility of using soil chemical extraction as a viable treatment technology for SAFR soil remediation. Through these test runs, the total percent metal removal efficiency and the number of stages needed to achieve optimal removal efficiency were established, as was the feasibility of full scale chemical extraction for the soils.

Several equations were developed to quantify the flow of solids, liquid, and metal into and out of each of the stages and around the system as a whole. Equation (7) calculates the solids (in mg) moving into or out of the system.

$$S_i, S_0 = S_c * V * UC_1 \qquad (7)$$

Where

S_i, S_o = solids input or solids output (*mg*)
S_c = solids concentration (*mg/L*)
UC_1 = volume unit conversion (*1 L/1000 ml*)
V = volume (*ml*)

Using the value from Equation (7), the quantity of liquid moving in and out of the system can be calculated as shown in Equation (8).

$$L_i, L_0 = (V * UC_3 * UC_4) - S_i, S_0 \qquad (8)$$

Where

L_i, L_o = liquid input or liquid output (*mg*)
UC_3 = volume/weight unit conversion (*1 g/1 ml*)
UC_4 = weight unit conversion (*1000 mg/1 g*)

Using the values S_i and S_0 from Equation (7), Equation (9) calculates the concentration of metal (in *mg*) in both the input and output solids.

$$M_{i,s}, M_{o,s} = C_i, C_o * UC_5 * S_i, S_o \qquad (9)$$

Where

$M_{i,s}, M_{o,s}$ = quantity of metal in solid (*mg*)
C_i, C_o = metal concentration in soil (*mg/kg*)
UC_5 = weight unit conversion (*1 kg/10^6 mg*)

Using the values L_i and L_0 from Equation (8), Equation (10) calculates the concentration of metal (in *mg*) in both the input and output liquid.

$$M_{i,L}, M_{o,L} = \left(C_{d,i}, C_{d,o}\right) * \left(L_i, L_0\right) * UC_6 * UC_7 \tag{10}$$

Where

$M_{i,L}, M_{o,L}$ = quantity of metal in liquid (*mg*)
$C_{d,i}, C_{d,o}$ = dissolved metal concentration in liquid (*mg/L*)
UC_6 = volume/weight unit conversion (*1 uL/mg*)
UC_7 = volume unit conversion (*1 L/10⁶ uL*)

Incorporating the values $M_{i,s}$ and $M_{o,s}$ from Equation (9), Equation (11) determines the percent metal removal efficiency based on the metal concentration of the input solids versus the output solids.

$$R_2 = \frac{M_{i,s} - M_{o,s}}{M_{i,s}} * 100 \tag{11}$$

Where

R_2 = percent removal extracted from soil (%)

Using these series of equations, the percent of metal removed from the feed soil was calculated.

In many instances, the inherent variability of the soil being fed to the CCME system produces a scattering of the results. This is highly evident when the CCME process is less effective. To resolve such data scattering problems, an alternative mass balance approach, which in less sensitive, was also utilized in the data interpretation scheme. This process is described in the following equations.

$$MR_L = FR_L * MC_L * UC_8 \tag{12}$$

Where

MR_L = Average weight of contaminant removed in the liquid
exiting the process (*mg/min*)
FR_L = Average liquid flow rate of the CCME Process (*mL/min*)
MC_L = Average CCME contaminant concentration at equilibrium (*mg/L*)
UC_8 = Volume unit conversion (*1L/1000mL*)

$$MF_S = FR_S * MS * MC_S * UC_9 \tag{13}$$

Where

MF_S = Average weight of contaminant fed to the CCME System (*mg/min*)
FR_S = Average flow rate of solids fed to the CCME System (*mL/min*)
MS = Average concentration of solids fed to the CCME System (*g/mL*)
MC_S = Average concentration of contaminant in the solids
fed to the CCME System (*mg/kg*)

UC_9 = Weight unit conversion (*1kg/1000g*)

$$R_3 = \frac{MR_L}{MR_S} * 100 \qquad (14)$$

Where

R_3 = Average calculated percent removal extracted from the soil (%)

These equations, while not as accurate as Equation 11, help smooth the data and allow a metals removal percentage to be calculated.

Training Center Cape May

Pilot-scale chemical extraction studies were conducted on the Cape May bulk soil. HNO_3 at the 0.05 M concentration and EDTA at the 0.05 M concentration were selected for CCME tests based on the results of the batch extraction tests. For both the HNO_3 and EDTA extractants, the condition of steady state is reached, which is important when evaluating the CCME removal efficiency. The CCME using EDTA approaches steady state at approximately four to eight hours after the start of the experimentation. More lead is removed in the liquid as it exits the system in Stage 4 than removed at Stage 1 (figure 15). This indicates that metals extraction is occurring in each stage when using the EDTA extract. The steady state effluent concentration for the EDTA extract is approximately 40 mg/l. In contrast, steady state is not approached until after ten to twelve hours after the start of experimentation for the HNO_3 extract. Results indicate that four stages may not be required for optimal extraction. It is also evident that the steady state effluent concentration (28-29 mg/l) is lower than that observed for EDTA.

Using a steady state removal of 40 mg/l and 25 mg/l for the EDTA and HNO_3 extracts, respectively, the lead removal from the soil is calculated using Equation 14 at 15% to 18%. This calculated lead removal reflects the data trends established during data analysis. These data indicate that the removal of lead from the Cape May soil using CCME is difficult. Based on these results, consideration of CCME treatment of the Cape May soil is not recommended.

Integrated Support Command Kodiak

Pilot-scale chemical extraction studies were conducted on Kodiak bulk soils. HNO_3 at the 0.05 M concentration and citric acid at the 0.05 M concentration were selected for CCME tests based on the results of the batch extraction tests. As with the Cape May soil, the condition of steady state is important when evaluating the removal efficiency of the CCME system. For both the HNO_3 and citric acid extractants, the condition of steady state was reached.

The CCME using HNO_3 approaches steady state at approximately eight to ten hours after the start of the experimentation. While the data is scattered, the general trend is that steady state effluent concentration for the EDTA extract is approximately 600 – 1000 mg/l. The data indicate that the general trend is for the soil's Pb concentration to decrease as the soil passes from Stage 4 (where the soil enters the system) to Stage 1. The concentration drops from over 16,000 mg/kg to 4000 mg/kg. Unlike the Cape May data, the percent Pb removal as calculated by Equation 11 for the HNO_3 extract is less scattered. As expected, based on the soil slurry concentration data,

the percent removal is quite high--varying between 73 to 84%. The Cu data also indicates that the removal of copper is 50 to 70%, which is quite high.
Steady state is achieved for the citric acid extract after four to eight hours following the start of experimentation. Results indicate that four stages may not be required for optimal extraction. It is also evident that the steady state effluent (400-500 mg/l) is lower than that observed for HNO_3. The data for the citric acid extract is much more scattered. The general trend observed is that the soil exiting the system has had little effect on reducing the Pb concentration. The present removal for the citric acid extract as calculated by equation 11 is probably less than 25%. Similar removals are observed for the Cu contaminant.

Using a steady state removal of 1000 mg/l and 500 mg/l for the HNO_3 and citric acid extracts, the percent lead removal from the soil is calculated using Equation 14 at 30% to 15%, respectively. This calculated lead removal reflects the data trends, but it is believed that it underestimates the removal of lead for the HNO_3 extractant. Based on these results, CCME treatment of the Kodiak soil is expected to be effective and is recommended for additional consideration.

Communications Station New Orleans

Pilot-scale chemical extraction studies were conducted on the New Orleans bulk soil sample. HNO_3 at the 0.05 M concentration and EDTA at the 0.05 M concentration were selected for CCME tests based on the results of the batch extraction tests. Like the Cape May and Kodiak soils, the condition of steady state is important when evaluating the removal efficiency of the CCME system. For both the HNO_3 and EDTA extractants, the condition of steady state is reached. The CCME using EDTA approaches steady state at approximately ten to twelve hours after the start of the experimentation. While the data is scattered, the general trend is that steady state effluent concentration for the EDTA extract is approximately 61-67 mg/l.

Similar data is observed for the HNO_3 equilibrium results. The condition of steady state is achieved after ten to twelve hours following the start of experimentation. The steady state effluent concentration for HNO_3 is only slightly lower than that observed with EDTA at 55–65 mg/l. It is also interesting to note that for both the EDTA and HNO_3 extracts, the Stage 2 effluent lead concentrations are higher than for Stage 3 or Stage 4, which is unexpected.

Data from the EDTA treated soil slurry concentration indicate that the soil's Pb concentration has decreased from 1000 mg/kg to approximately 200 mg/kg as a result of CCME treatment. This represents substantial lead removal. The twelve-hour data as calculated by Equation 11 for the EDTA extract indicates that little lead removal is occurring after the first stage. This means that for the EDTA extract, only one to two stages may be required to achieve optimal removal (76%). Due to the low concentration of the other metals found in the New Orleans soil, the percent removal results for the other metals are highly scattered and provide little insight for treatment. While the data are scattered, the general trend for the HNO_3 extract as observed in the twelve-hour data is for the soil concentration to decrease as the soil progresses up from Stage 4 to Stage 1. These data also indicate that all four stages are required to achieve optimal removal. The removal for the HNO_3 extract as calculated by equation 11 ranges between 63 to 76%.

Using a steady state removal of 60 mg/l and 55 mg/l for the EDTA and HNO_3 extracts, respectively, the lead removal from the soil is calculated using equation 14 at 30% to 27%.

These numbers underestimate the lead removals shown in the data, and based on the soil lead concentrations, it is believed that the higher lead removals are more accurate. Based on the CCME results, treatment of the New Orleans soil pile materials using chemical extraction is recommended for additional consideration.

Summary of the Chemical Extraction Results

Three USCG SAFR soils were subjected to the chemical extraction tests (Cape May, Kodiak, and New Orleans). Ketchikan soils were not tested in the chemical extraction study due to the soils' very fibrous composition that could not be processed through either the pilot or full-scale equipment. Results for this test indicate that full-scale chemical extraction has the potential to be effective for the ISC Kodiak and New Orleans soil but not the Cape May soil. Based on the CCME test results and experience with full-scale soil washing processes, nitric acid is the recommended extract, although the leaching of nitrates from the treated soil must be considered as a possible environmental problem.

Electrokinetic Investigations

Enhanced electrokinetic (EK) remediation tests were performed in an attempt to move the metal contaminants in the soil under the influence of an applied electric field. All EK tests conformed to the procedures outlined in the Material and Methods section of this report.

Selection of Enhancement Agent

The enhancement agents selected for evaluation were based on the results obtained from the batch chemical extraction test conducted as part of this study for the Cape May and Ketchikan soils. Nitric acid, EDTA, and citric acid were identified as the most effective metal removers of lead for these soils. Batch chemical extraction tests were not performed for the Ketchikan soils; but nitric acid, citric acid, and EDTA were selected for the EK study. The extracting agents utilized in all EK bench-scale evaluations are presented in table 15.

Table 15. Extractants utilized in EK bench scale tests.

Test ID (Soil, Series #)	Extraction Agent Utilized	Molar Concentration
Cape May	Nitric Acid: Cathode	0.1
Cape May	Citric Acid: Cathode	0.25
Cape May	Citric Acid: Cathode/EDTA: Anode	0.25/0.05
Ketchikan	Nitric Acid: Cathode	0.1
Ketchikan	Citric Acid: Cathode/EDTA: Anode	0.25/0.05
Kodiak	Nitric Acid: Cathode	0.1
Kodiak	Citric Acid: Cathode/EDTA: Anode	0.25/0.05

The EDTA/citric acid studies were conducted by using citric acid as the cathode-half-cell pH control agent and EDTA as the metal chelating agent that should be transported across the soil through electrokinetic phenomena, as discussed earlier. The molar strength of the enhancements agents for the anode amendment were determined in the batch chemical extraction study as the molarity that removed the lead most effectively. The strength of the cathode amendment was not critical because the quantity of acid to be added in the experiment was determined by the rate of OH⁻ production. Based on past operating experience, molar strengths of 0.25M for citric acid and 0.1M for nitric acid were selected for this study.

Contaminant Baseline Determination

A contaminant baseline was conducted for all of the EK bench scale tests. As shown in table 16, the baselines for the Cape May and ISC Kodiak soil were more constant than that observed for the ISC Ketchikan soil. Results for cadmium, chrome, and zinc are not presented due to the relative low concentration of these contaminants.

Table 16. Metal contaminant baseline concentrations for USCG EK bench scale tests.

Soil Type, Replicate	Pb (mg/kg)	Cu (mg/kg)
Cape May A	481	37.4
Cape May B	682	35.7
Cape May C	523	49.7
Cape May D	529	35.2
Cape May E	612	33.8
Average	**565**	**38**
Ketchikan A	12533	592
Ketchikan B	11579	699
Ketchikan C	11172	573
Ketchikan D	14156	597
Ketchikan E	25664	446
Average	**12756**	**588**
Kodiak A	18002	1026
Kodiak B	19757	487
Kodiak C	20824	526
Kodiak D	19753	1802
Kodiak E	19552	737
Average	**19459**	**763**

Electrokinetic Results

Various data are presented in an attempt to describe heavy metal removal from the soils under enhanced electrokinetic conditions. Soil metal removal is judged to be the most important consideration. However, other factors such as runtime pH, post-run soil pH, electro-osmotic flow, applied voltage, and energy expenditure must be described if a full understanding of the dynamics of the systems are to be understood. The results obtained for Cape May, Ketchikan, and Kodiak are discussed in the following sections. Equations, theories, and assumptions utilized in the formulation of the data are presented in the Cape May results section. These ideas are consistent in the formulation of the results for the other two soils.

The EK experiments for all soils were conducted for approximately 41 days (1000 hrs). While longer treatment periods may be required for complete removal of the contaminants, it was believed (based on experience) that the 41 day period should provide enough time to determine if EK treatment could move the contaminants and have the potential as a successful treatment.

Training Center Cape May

Runtime pH

The half-cell anode and cathode pH were monitored throughout the EK experiment to gain knowledge of parameters with respect to electrode interfacial pH. Figures 23 and 24 show the average anode and cathode pH for the three EK tests that were performed on the Cape May soil.
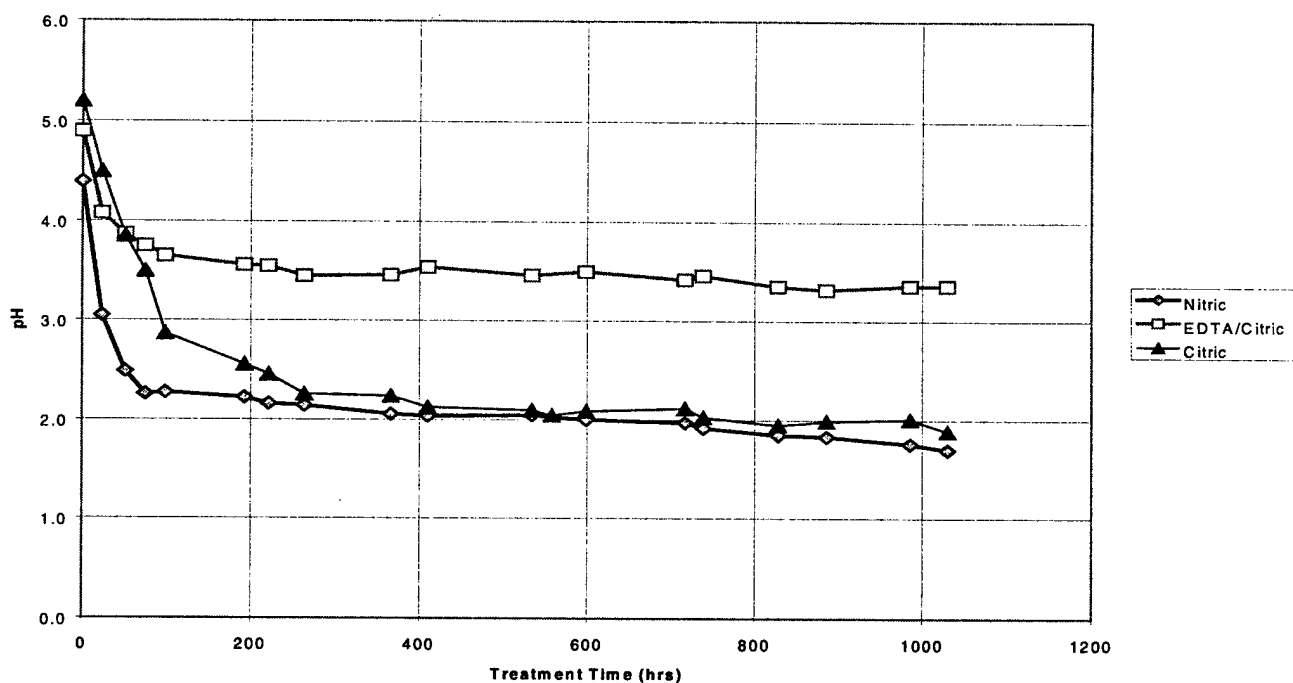

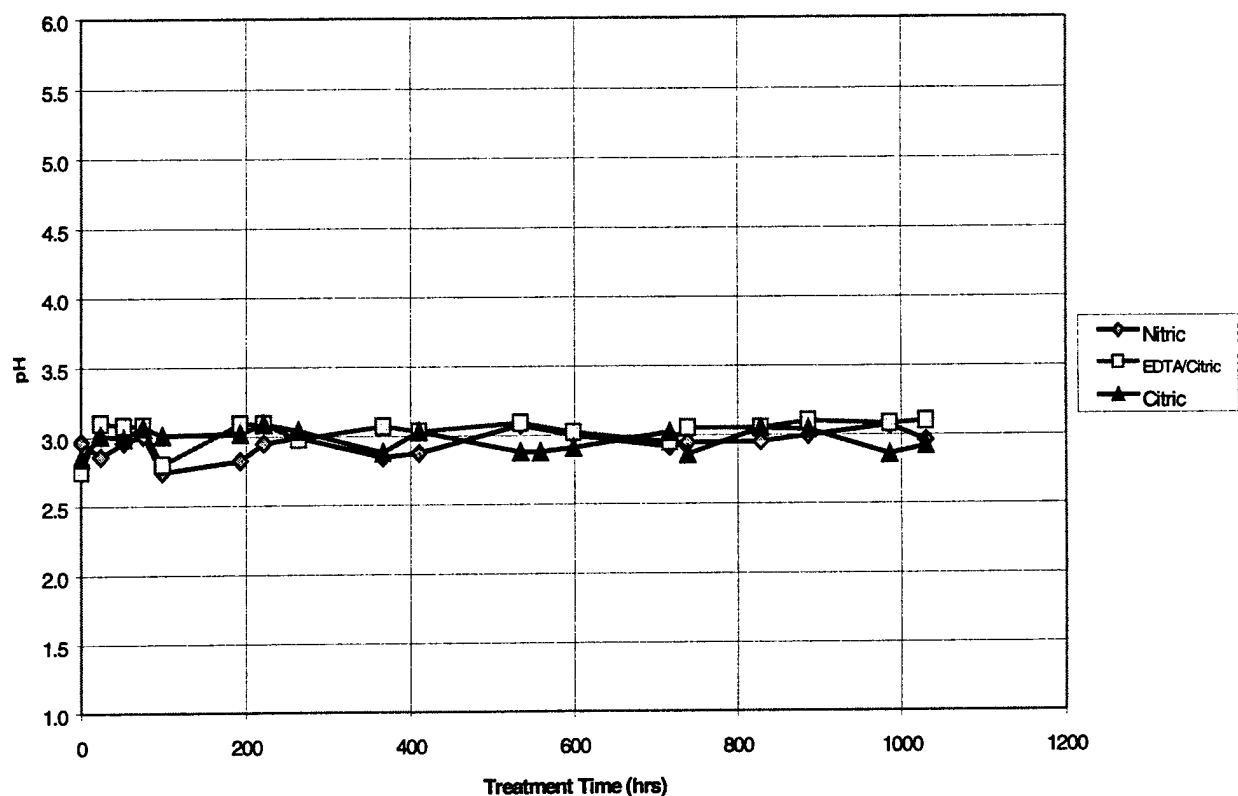Figure 23. Anolyte pH for the Cape May SAFR soil.

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Figure 24. Catholyte pH for the Cape May SAFR soil.

The anode results show a sharp decrease until a process time of approximately 100 hours. After this treatment period, the slope of the pH decrease is much less. This decrease in the pH is attributed to the production of H^+ ions at the anode. It is clear in figure 23 that the pH of the EDTA/citric system is maintained at a higher pH than that of amended systems, which only used acids (nitric acid & citric acid). The cathode pH of the three EK tests for the Cape May soil were maintained at or slightly below a pH of three by the implementation of enhancement agents (nitric acid & citric acid). Figure 24 indicates that, as expected, the control of the pH was quite good throughout the duration of the tests.

Electro-osmotic Flow

Figure 25 presents the cumulative electro-osmostic (EO) flow for the three Cape May EK tests. It can be seen that in the citric acid and citric/EDTA amended tests the cumulative EO flow was high. The citric acid amended test had more than 40 liters of EO flow after 1000 hours of treatment while the citric acid/EDTA amended test had only 5 liters of EO flow after 1000 hours of treatment. In contrast, the nitric acid amended test had very little EO flow.

Applied Voltage

The voltages across the cells are dependent upon the resistance created across the samples by the applied constant current. It was the initial intent for each test to be run at constant current. Under the conditions of constant current, a change in system resistance would result in a change in applied voltage only, as explained by Ohm's law (V = IR). For the nitric and citric/EDTA amended test, the current was held constant between 36-38 amps; thus the voltage varies. In

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contrast, the power supply for the citric acid amended cell malfunctioned. For this cell, the system was run at a constant voltage of approximately 138 volts, and the current varied as the test progressed. The voltages observed for the nitric acid and citric/EDTA experiments rapidly decreased after the initial start of the test to values of approximately 5 and 120 volts, respectively, and remained constant for the duration of the experiments. This trend was predicted by Acar et al. (1995) as a result of cathode depolarization.
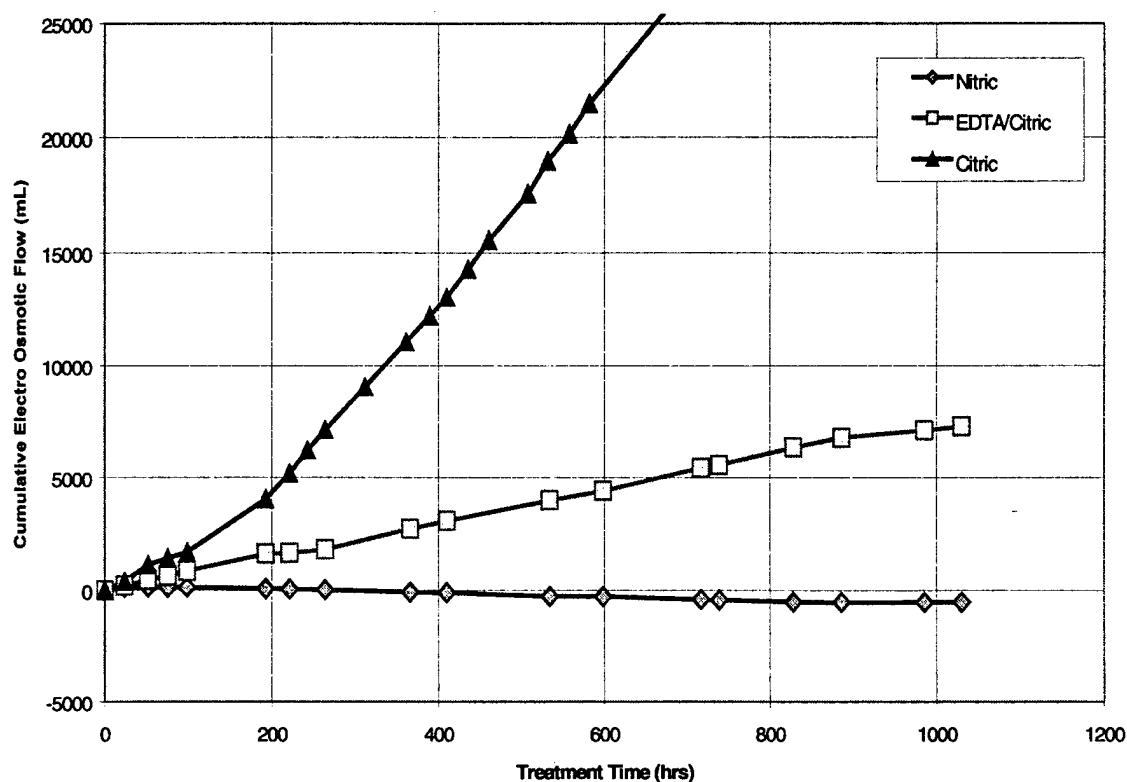

Figure 25. Cumulative electro-osmotic flow for the Cape May

Anode/Cathode Daily Liquid Results

Over the course of the experimental runs, samples of the cathode and anode solutions were collected and analyzed for the contaminants of concern. As reported earlier, only lead and copper results are discussed because of the low concentrations of the other contaminants. For the nitric acid, amended test replicates were run. For the nitric acid amended cell, the catholyte concentration approaches a maximum of about 40 mg of lead in solution. The anolyte for the replicate cells provides conflicting results. Cell B indicates that very little lead is measured in the anolyte while, for Cell A, over 100 mg of lead is measured in the anolyte. Results for the citric acid/EDTA amended cell indicate that even more lead was detected in the anolyte, 200 to 300 mg. In contrast, very little lead was measured in the citric acid amended cell. Although the concentrations for copper are much smaller, similar trends are observed.

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Metal Post Run Soil Results

There are several methods in presenting the results of EK experiments, but it is believed that a mass balance approach is the most useful method in understanding how effective the EK process was for a particular soil. The following paragraphs are an attempt to clarify the mass balance approach. This discussion is followed by an explanation of the experimental results for the three EK Cape May experiments. For this discussion, figure 26 will be used for illustration purposes to clarify the data handling procedures.
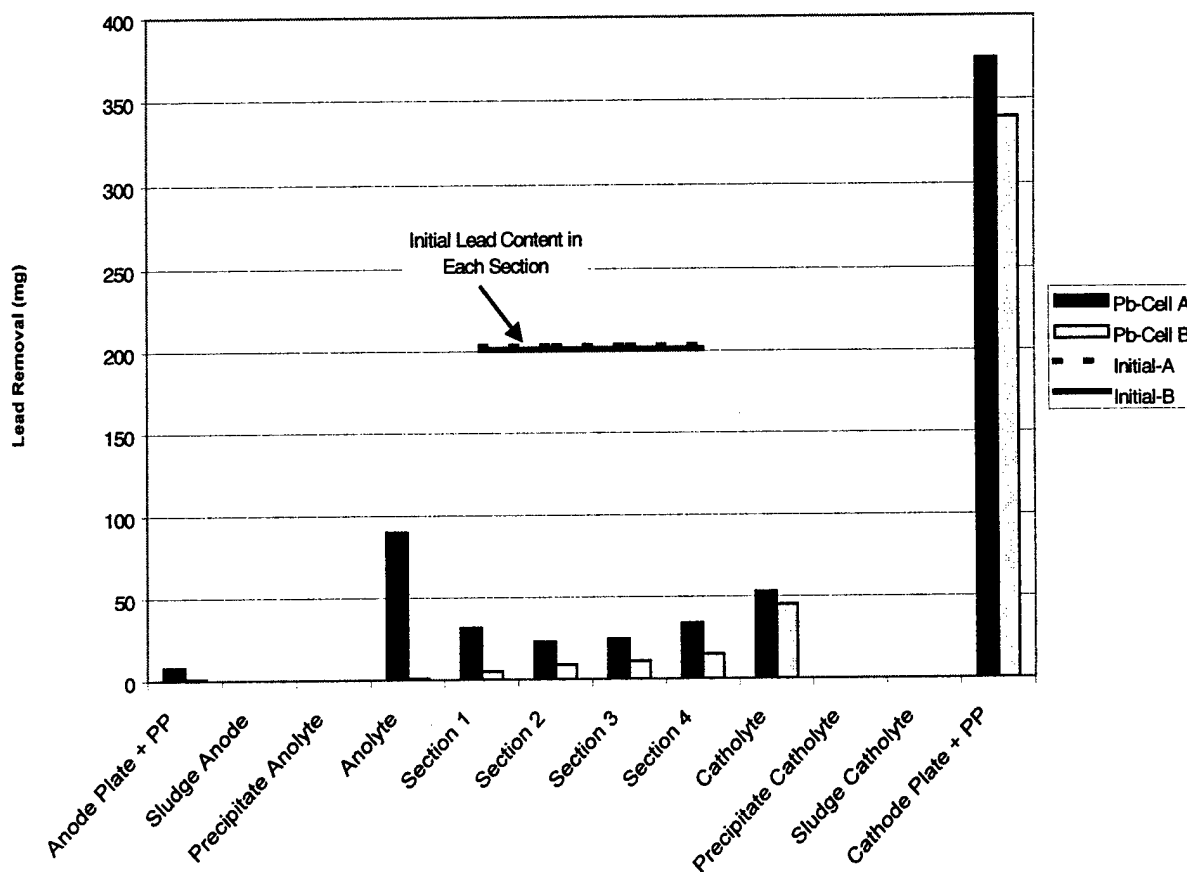

Figure 26. Cape May nitric acid amended lead mass balance results.

The straight lines at 203 mg and 201 mg (for cell A and B) presented in figure 26 (identified as the initial lead) correspond to the amount of metal contained in each soil section before initiation of the test. For example, the figure shows an initial lead value of approximately 203 mg for cell A. This value corresponds to 203 mg of lead contained in each soil section; and, since the cell was divided into four sections, this results in a total of 812 mg of lead contained in the approximate 1.5 kg specimen before EK treatment was initiated. The bars illustrate the post-run heavy metal gradient of the EK treated soil. The amount of initial and post-run heavy metals were determined by the following equation:

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$$M_{mass} = (C_{AA} \bullet W_{soil}) \tag{15}$$

where:

M_{mass} = the amount of heavy metal (initial or final) in milligrams.
C_{AA} = the metal concentration determined by atomic absorption
       spectroscopy (AAS) in mg/kg.
W_{soil} = the dry weight of soil in the test in milligrams.

The replicates conducted only for the nitrate amendment are presented to compare and contrast any significant variation between duplicate tests.

The information provided on the x-axis of each metal graph correspond to the various area where metal could be found in the experimental cell and supporting vessels. Summation of the metal found in the various locations presented on the x-axis accounts for all metal movement (or non-movement). "Anode Plate + PP" and "Cathode Plate + PP" correspond to the amount of post-treatment metal found electro-deposited on the anode and cathode electrodes, respectively, and their pressure plates. "Sludge Anode" and "Sludge Catholyte" correspond to any metal found in the sludge (or precipitate) contained in the post-run anode and cathode half-cell precipitant. "Precipitate Anolyte" and "Precipitate Catholyte" correspond to the metal analysis conducted on precipitant collected in the anode and/or cathode re-circulation tanks (if any) during actual treatment of the soil. "Anolyte" and "Catholyte" are measures of the metals found in the analysis of daily liquid samples. "Section 1," "Section 2," "Section 3," and "Section 4" correspond to the post-run soil analysis conducted in the soil specimens. "Section 1" is identified with the soil that is closest to the anode half-cell compartment, and "Section 4" relates to the soil closest to the cathode half-cell (refer to figure 16).

The Cape May Pb(II) removal results for the nitric acid amended, citric acid amended, and citric/EDTA amended tests are given in figures 26, 27, and 28, respectively. For the nitric acid amended tests in figure 26, over 87% of the total amount of lead contained in the system is removed from the soil, and 43% of lead is accumulated in the section nearest the cathode. Similar results are observed for the citric acid and citric/EDTA amended tests at 59% and 81% total removal, respectively. Lead was observed electroplated on the cathode electrode and pressure plate. This suggests that the major transport mechanism is electromigration. For all Cape May EK tests, a large percentage of lead is plated on the electrode. Figure 27 for the citric acid amended cell shows an increase in lead from Section 1 to Section 4. Prior to EK testing, the concentration of lead should be relatively constant throughout the sections because the soil was homogenized prior to placing it in the cell. The nitric acid and citric acid/EDAT amended tests do not have as pronounced a trend as observed for the citric acid test. This is because more lead has been moved out of these systems (figure 27), and it is expected that the nitric acid amended cell is approaching the limit of removal of lead with 3 mg/kg remaining in the soil in Section 1. It also interesting to note that the critic acid/EDTA amended cell has the largest amount of lead in the anolyte of the three amendments' tests. It is expected that EDTA produces a negative lead complex which is removed at the anode. Ranking the EK amendments for the Cape May soil for lead removal generates the following: nitric acid > citric acid/EDTA > citric acid.
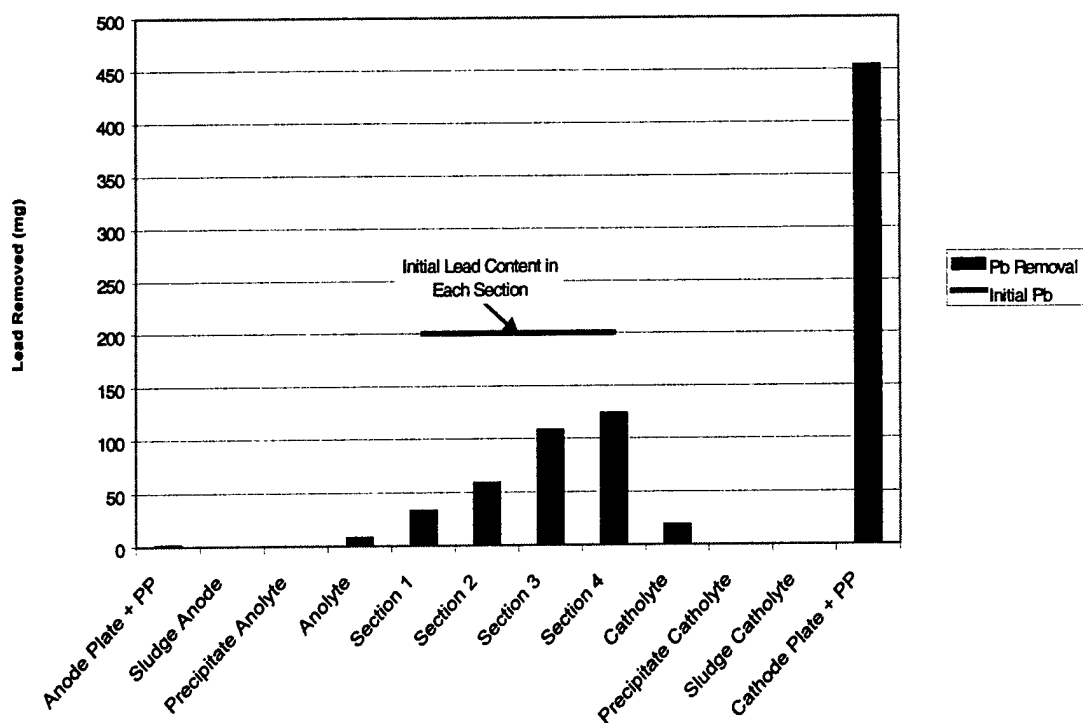
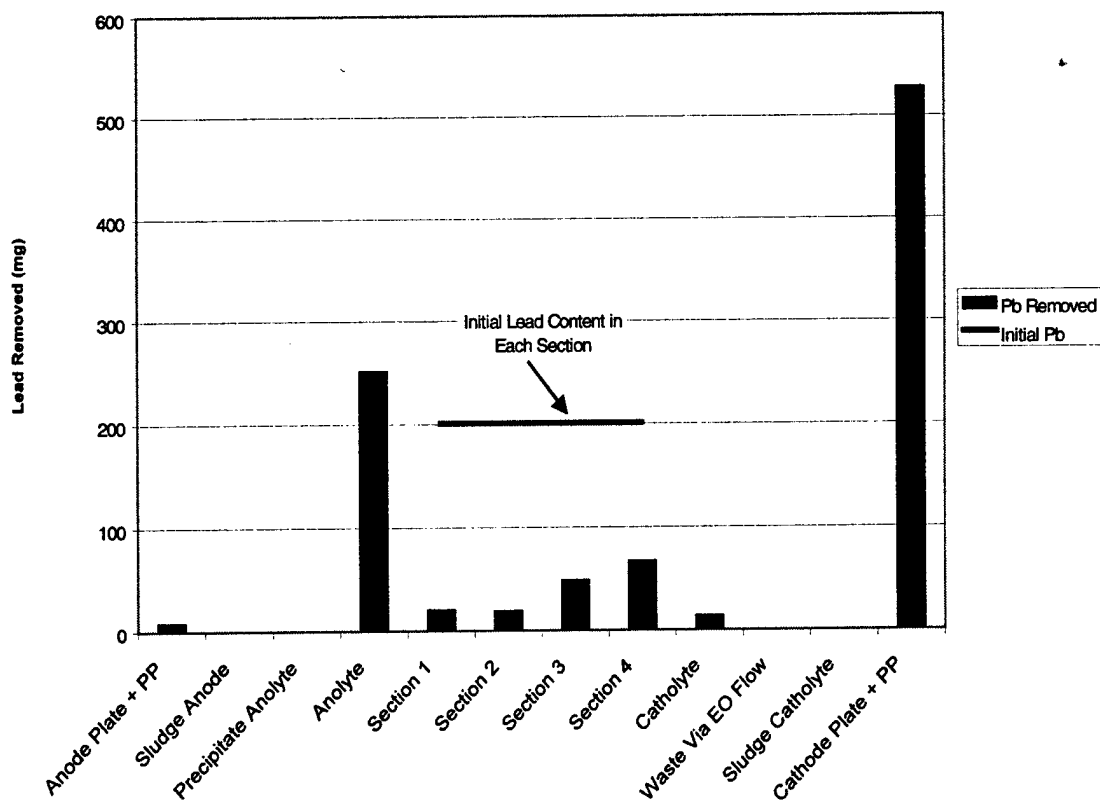Figure 27. Cape May citric acid amended lead mass balance results.

Figure 28. Cape May citric acid/EDTA amended lead mass balance results.

Results for the copper soil contaminant were similar to those observed for lead, although the soil concentration of copper is much lower than that of lead. A large percentage of copper is removed from the soil, and a great deal of copper is being plated on the electrode. As observed for the lead contaminant, the nitric acid amendment is the most effective in moving the copper, but citric acid appears to be more effective than the citric/EDTA combination. The results for the citric acid/EDTA amended test indicate that most of the Cu is concentrating in Section 4, and it has not removed from the soil and plated on the electrode.

Energy Expenditure

The average cumulative energy requirements for the three Cape May EK tests are plotted versus the treatment time. The energy was calculated at discrete points throughout the duration of each test and summed to achieve a cumulative value of total energy utilized. The energy obtained at a discrete point was calculated using the equation:

$$E_{point} = (((V_{point} \bullet A_{point}) \bullet T) / V_S) \bullet C_F \qquad (16)$$

where:

E_{point} = the energy at a specific sampling period in kW-h/cubic meter.
V_{point} = the voltage at a specific sampling period in volts.
A_{point} = the amperage at a specific sampling period in amps.
T = the time of sampling in hours.
V_S = the total volume of the sample in cubic meters.
C_F = a dimensionless correction factor (1000).

As shown in figure 29, the order of increasing energy expenditure for the EK remediation tests conducted on Cap May soil was determined to be nitric acid > citric/EDTA > citric acid.
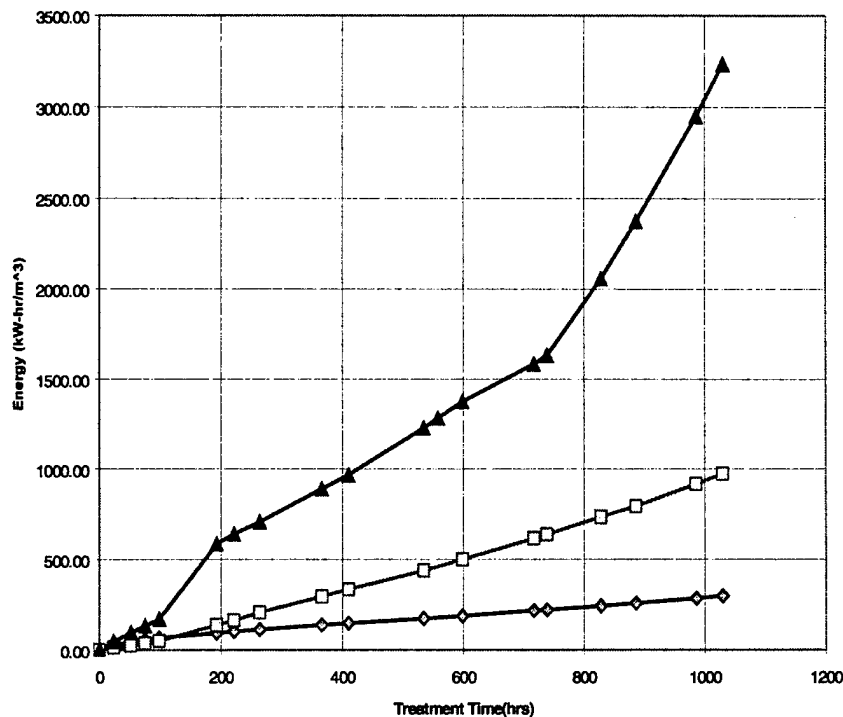

Figure 29. Cumulative energy expenditures for the EK treated Cape May soil.

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Using the information presented in the figure and a power cost of one kW-hour = $0.07, the power cost to remove 87% of the lead using nitric acid as an amendment is estimated to be $20/m³. Other costs, which include chemical, operating, and capital must also be considered; but these EK treatment processes are effective and cost competitive.

Integrated Support Command Ketchikan

Runtime pH

Figure 30 presents the average anode and cathode pH for the two EK tests that were performed on the Ketchikan SAFR soil. The pH results show a sharp decreasing pH until a process time of approximately 100 hours is achieved. After this treatment period, the slope of the pH decrease is much less. It is clear in the figure that the pH of the cathodes (pH = 3.3 – 5.1) are maintained at a higher pH than the anodes (pH = 2.0 – 4.0). The pH controls for the catholyte of the two EK tests were not as tight as exhibited for the Cape May soil. The pH at the cathode varies over two pH units but is maintained below three for most of the experiment.
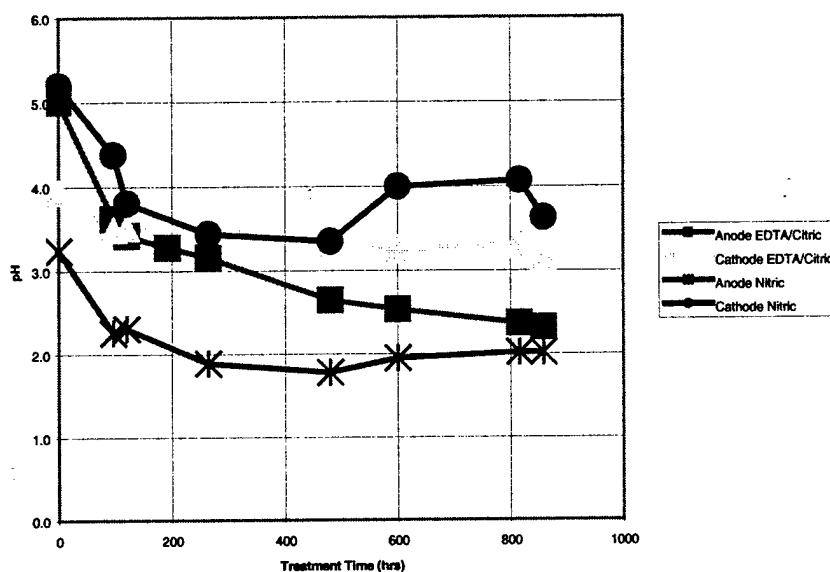
Figure 30. Anolyte and catholyte pH for the Ketchikan SAFR soil.

Electro-osmotic Flow

The cumulative electro-osmotic (EO) flow for the two Ketchikan EK tests was much lower than the Cape May EK experiments. In fact, the maximum cumulative flow is less than 2,500 ml. For the Cape May soil, EO flow exceeds 40,000 ml. Based on these results, little EO flow is expected to be observed for EK treatment of the Ketchikan soil in the field.

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Applied Voltage

Online voltage probe readings for each individual test cell show an online voltage profile across the specimens, as well as electrical gradient curves. For the Ketchikan EK tests, the current was held constant at about 27 amps, and the voltage is allowed to vary. The voltage required by both cells is quite minimal. After an initial equilibrating period of about 100 hours, the voltage remains relatively constant, varying from four to nine volts for the test period.

Post-Run pH Profile

The post-run pH of the specimen was measured to illustrate the pH gradient created across the soil due to the migration of the H^+ ion front and the application of pH control to the cathode compartment. The post-run pH profiles for the Ketchikan soil show that the pH front moved through the entire mass of the soil, resulting in a low pH in each soil section.

Anode/Cathode Daily Liquid Results

The concentration of the catholyte lead contaminant extracted for the two runs approached a maximum of about 1200 to 1500 mg of lead in solution. The anolyte concentrations were much lower. The nitric acid amended cell had a maximum anolyte concentration of 65 mg. As expected, the EDTA amended anolyte extracted more lead (300 mg) due to the formation of negatively charged lead complexes, but these values were much lower than observed at the cathode. Similar trends were also observed with the copper contaminant. The catholyte had larger amounts of copper than the anolyte. Overall the copper content of the Ketchikan soil was much lower than lead, but EK moved copper into the cathode compartment of the cells.

Metal Post Run Soil Results

The Ketchikan Pb(II) removal results for the nitric acid amended and citric/EDTA amended tests are given in figure 31. It can be seen that over 71.6% of the total lead contained in the system is removed from the soil, and 88% of this lead accumulated in the section nearest the cathode for the nitric acid amended tests. Similar results are observed for the citric/EDTA amended tests at 62.5% total lead removal. A large amount of lead was observed electroplated on the cathode electrode and pressure plate when compared to the anode. This suggests that the major transport mechanism is electromigration. Figure 31 shows an increasing trend for lead from Section 1 to Section 4. Prior to EK testing, the concentration of lead should be relatively constant throughout the because the soil was homogenized prior to placing it in the cell. As expected, the largest amount of lead was found plated at the anode in the EDTA/citric acid amended EK test. As discussed previously, it is expected that EDTA produces a negative lead complex which is removed at the anode. For the Ketchikan soil, the nitric acid appears to be only slightly more effective in removing lead than the EDTA/citric acid amended test, but both tests show good lead mobilization and removal.

The results for the Ketchikan copper analysis for the two amendments are presented in figure 32. Results similar to lead were observed for the copper soil contaminant, although the soil concentration of copper is much lower than for lead. The nitric acid amendment appears to be more effective than the EDTA/citric acid amended test in removing copper.
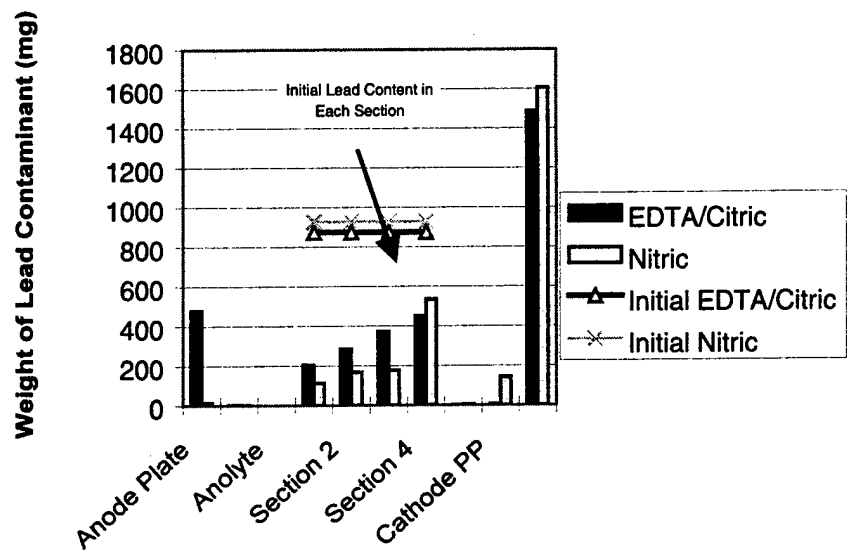
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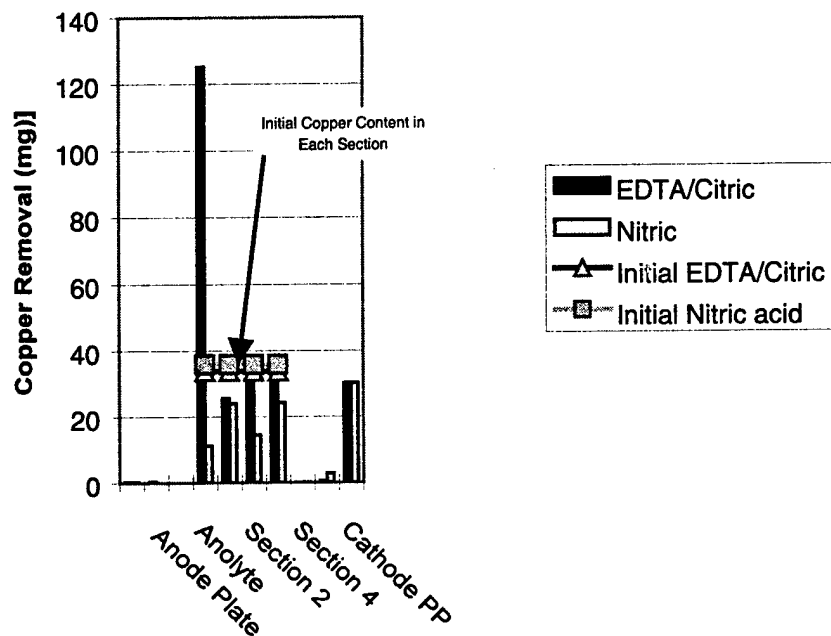Figure 31. Ketchikan lead mass balance results.

Figure 32. Ketchikan copper mass balance results.

Energy Expenditure

The average cumulative energy requirements for the two Ketchikan EK tests were plotted versus the treatment time. The nitric acid amended cell requires slightly less power (155 kW-hr/m^3) than the citric acid/EDTA amended cell (250 kW-hr/m^3) but achieves a higher removal (71%). Using the recorded information and an energy cost of one kW-hour = $0.07, the total power cost to remove 71.6% of the lead using nitric acid as an amendment is estimated at $11/m^3. Other costs, which include chemical, operating, and capital must also be considered; but, based on power costs, these EK treatment processes are effective and cost competitive.

Integrated Support Command Kodiak

Runtime pH

Figure 33 presents the average anode and cathode pH for the two EK tests that were performed on the Kodiak SAFR soil. The pH results show a sharp decreasing pH until a process time of approximately 100 hours is reached. After 100 hours of treatment time, the pH decrease is much less. The pH of the electrolytes were maintained between 1.5 to 3.6. The pH control for the catholyte of the two EK tests for the Kodiak was quite good. The pH at the cathode does not vary over 0.5 pH units after the first 100 hours of treatment.
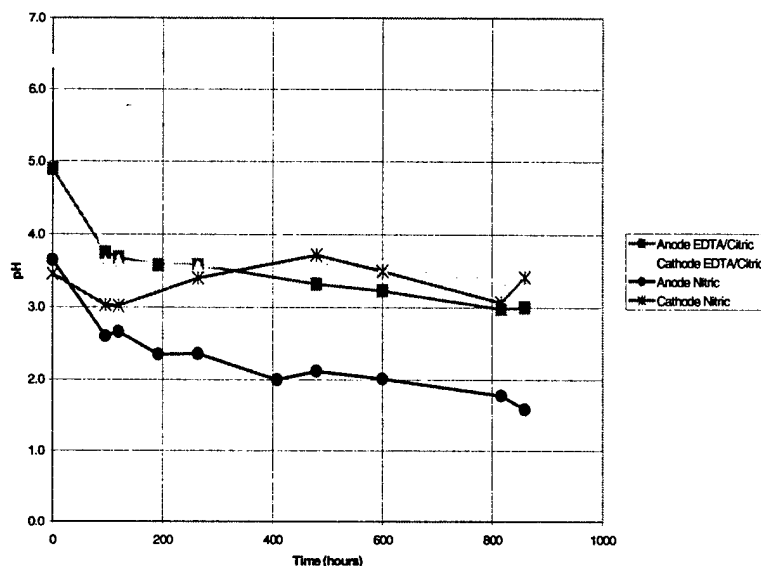

Figure 33. Anolyte and catholyte pH for the Kodiak SAFR soil.

Electro-osmotic Flow

The Kodiak EO flow was much lower when compared to the Cape May EK experiments. Based on these results, little EO flow is expected to be observed for the Kodiak soil in the field.

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Applied Voltage

Online voltage probe readings for each individual test cell show an online voltage profile across the specimens, as well as electrical gradient curves. For the Kodiak EK tests, an attempt was made to hold the current constant at 28 mA, and the voltage is allowed to vary. For the EDTA/citric acid amended cell this was the case, but for the nitric acid amendment, some variation in the current was observed. The voltage required by both cells was higher than that required for the Cape May or Ketchikan soils. After an initial equilibrating period of about 100 hours, the voltage remains slowly increased to about 50 V for the EDTA/citric acid amended test and was at a relatively constant 140 V for the nitric acid amended test, except at the end of the test.

Post-Run pH Profile

The post-run pH of the specimen was measured to illustrate the pH gradient across the soil due to the migration of the H^+ ion front and the application of pH control to the cathode compartment. The data show that the pH front did not completely move through the soil mass. There was a steady increase when moving from the soil sections near the anode towards the cathode. The pH of the treated soil varies from a low of 3.8 to a high of 5.7, which is approaching the untreated soil's pH of 5.8.

Anode/Cathode Daily Liquid Results

Figure 34 presents the anolyte and catholyte lead contaminant extracted for the two experimental EK runs for the Kodiak soil. As shown by this figure, the catholyte concentration approaches a maximum of about 550 to 650 mg of lead in solution for the EDTA/citric acid amendment. The EDTA/citric acid amended anolyte also has a higher lead content than that measured for the nitric acid amended treatment. As expected, the EDTA amended anolyte extracts more lead (at 575 mg) due to the formation of negatively charged lead complexes. It was also expected that the concentration of lead in the anolytes would be much higher due to the large amount of lead found in the Kodiak soil. Very little copper was measured in the anolytes of the Kodiak EK treated soil. The maximum mass of copper extracted is measured in the cathode of the nitric acid amended test as less than 10 mg.

Metal Post Run Soil Results

The Kodiak Pb removal results for the nitric acid amended, and citric/EDTA amended tests are given in figure 35. It can be seen that only 5.4% of the total lead contained in the system is removed from the soil for the nitric acid amended test. Similar results are observed for the citric/EDTA amended tests at 0.08% total lead removal. The electrode and pressure plates were relatively clean, indicating that very little plating had occurred. While little removal was observed, Figure 35 shows an increasing trend for lead from Section 1 to Section 4 for both tests. It appears that the nitric acid amendment has moved more of the lead to Section 4 than the EDTA/citric acid amendment. The EDTA/citric acid amended test has accumulated more of the lead in Section 3, so the amendment is moving the lead at a slower rate. It would be expected that if this experiment were conducted longer than the 900-hour test period, eventually the lead would move from Section 4 into the catholyte and possibly be plated on the surface of the cathode.
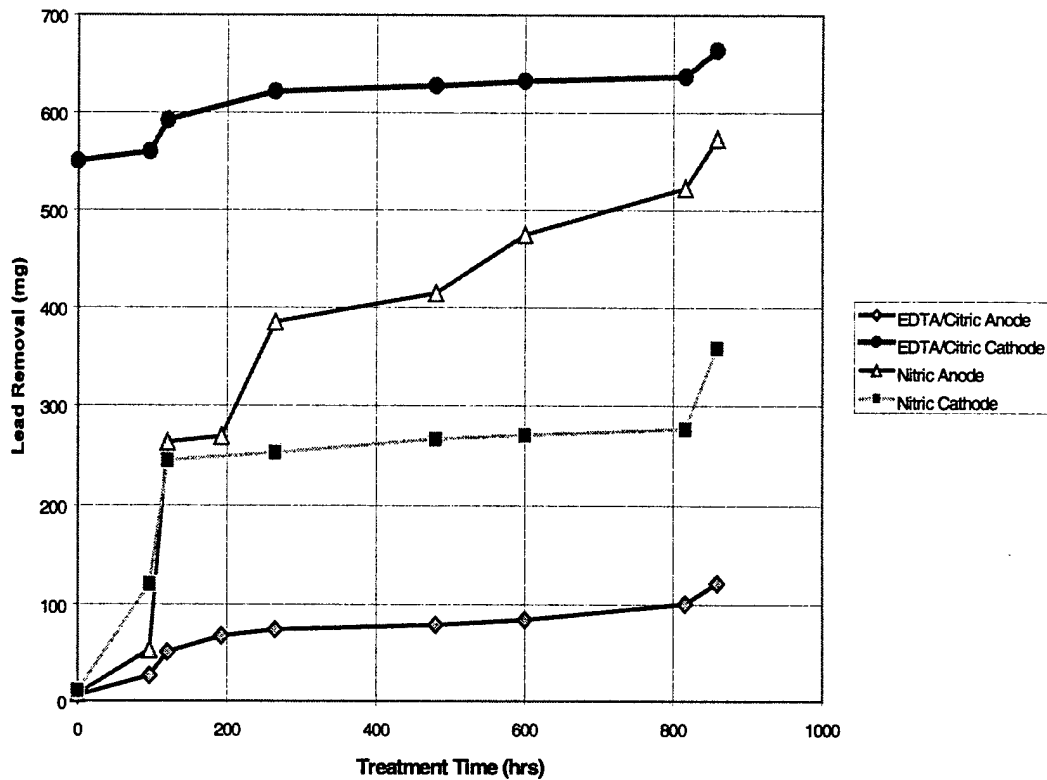
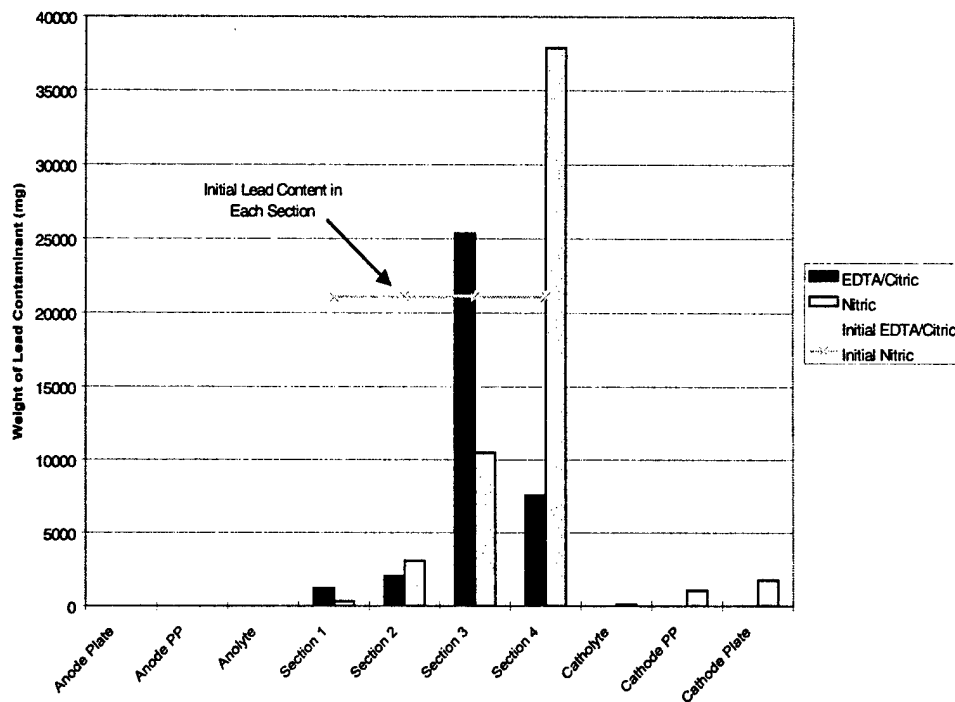Figure 34. Kodiak EK daily liquid sample analysis for the lead contaminant.

Figure 35. Kodiak lead mass balance results.

The results for the copper analysis for the two amendments show very little movement of the copper. Most of the copper movement appears to be towards the anode (Section 1) for the EDTA/citric acid amended test. Some discretion must be used when interpreting this data because more copper was measured in each cell section after treatment than originally placed in each section of the cell.

Energy Expenditure

The average cumulative energy requirements for the two Kodiak EK tests were plotted versus the treatment time. The nitric acid amended cell required much more power (2600 kW-hr/m^3) than the citric acid/EDTA amended cell (1170 kW-hr/m^3). While greater lead movement was observed for the nitric acid amendment, the power required for this treatment is twice as high. Using a power requirement of 1170 kW-hr/m^3 and an energy cost of one kW-hour = $0.07, the total power cost for the EDTA/citric acid amended test is estimated at $82/m^3. Other costs, which include chemical, operating, and capital must also be considered; but, based on power costs, these EK treatment processes are considered to be quite costly.

Conclusions and Recommendations

Conclusions

The purpose of this study was to identify and investigate technologies that may be effective in reducing any possible environmental impact of soil contaminants resulting from current or past USCG SAFR activities. The results of this study indicate lead was measured at levels of concern in all of the USCG sites sampled. Remediation of these ranges may or may not be required under current regulations, but Pb is present at levels that may adversely impact the environment as a result of SAFR activities.

Soil remediation technologies were the focus of this investigation. These metal remediation technologies targeted the reduction of contaminated soil mass. This is accomplished by either producing a small, highly concentrated contaminated residual and a clean large volume soil mass or through the removal of the soil's contaminants in their entirety.

Both physical separation and extraction technologies appeared to have merit when applied to the four USCG soils. Physical separation and chemical extraction were not effective for all four soils, but each technology was effective for at least one of the soils tested. Only the EK remediation technology appears to be effective for all soils. Regardless of the technology applied, all the technologies will produce a metal contaminated residual that will require disposal or additional treatment. The volume of this residual produced will depend on the technology applied and the amount of contamination in the soil.

Specific conclusions regarding the various tests performed in this study are presented below.

Core and Surface Sample Analysis

While it was not the intent of this study to characterize USCG contaminants at SAFRs for regulatory purposes, sampling at the four sites indicated that substantial quantities of lead were found at these sites. Based on the results of this study, the SAFRs at Cape May, Ketchikan, and New Orleans all have unique issues which may require these ranges to fall under current regulatory criteria. These issues include:

- Cape May has a berm that is no longer utilized as an impact area to stop bullets and is heavily contaminated with lead.
- New Orleans has a waste pile that most likely requires some action. This waste pile also has substantial contamination.
- Ketchikan has a range that is no longer in use and has lead that may be migrating from the range.

Lead appears to be the main contaminant of concern at these USCG SAFRs.

Bulk Sample Analysis and Characterization

As a result of the bulk sample characterization and testing, which includes chemical analysis, TCLP analysis, buffering capacity studies, and particle density analysis, the following conclusions are provided.

- The bulk samples were representative of soils at the four USCG SAFR sites.
- TCLP analysis indicates that all four soils fail the TCLP test for lead.
- The New Orleans SAFR soil has a relatively high buffering capacity (acid neutralization capacity) while the Ketchikan soil has a low buffering capacity when compared to other military soils.
- The particle density of the Ketchikan soil is low.

Physical Separation Tests

Physical separation is a process that attempts to separate the soil into various fractions by capitalizing on differences in particle size, density, surface properties, or other differing soil factors.

- Physical separation technologies were effective for treating the Cape May soil. Wet sieve separation and tabling concentrates over 70% of the soil mass into fractions that can be separated to produce a soil with low concentrations of lead.
- Attrition tends to improve the effects of physical separation for the Cape May Soil.
- Physical separation processes were only moderately effective for the New Orleans soil.
- Physical separation processes were ineffective for the Kodiak soil, and cannot be applied to the Ketchikan soils cost-effectively.

Chemical Extraction Soil Tests

Chemical extraction is a process in which a contaminated soil is contacted with an extracting agent or solvent that is capable of solubilizing the metal contaminant from the soil particle.

- Over 99% of the lead measured in the Kodiak soils was extracted under optimal conditions. EDTA, NTA, HCl, and HNO3 were the most effective reagents for removing lead from the soil. In contrast, chemical extraction under optimal conditions was not effective for the New Orleans soil.
- In contrast to the optimal condition test results, the twelve hour pilot-scale soil washing studies indicate the chemical extraction could be effective for the Kodiak and New Orleans soils but not the Cape May soil.
- The pilot-scale counter-current metal extraction (CCME) studies indicated that three to four stages are needed to achieve maximum Pb removal.
- A thirty-minute acid contact period is appropriate for the treatment of the Kodiak and Cape May soils.
- Over 80% removal of the lead from the Kodiak soil and 70% from the New Orleans soil can be achieved with CCME.

- Nitric acid is recommended for use as an extract solution if soil washing is applied at the USCG facilities.

Electrokinetics

Enhanced electrokinetic (EK) remediation tests were performed as part of this study in an attempt to move the metal contaminants in the soil under the influence of an applied electric field.

- EK is effective for the Cape May, Ketchikan, and Kodiak soils. Although not subjected to the EK evaluations, it is anticipated that EK will be effective in removing lead from the New Orleans soil.
- EK treatment was most effective for the Cape May and Kodiak soils. While not as effective EK efficiently moved the lead in the Ketchikan soil.
- While EK technologies are young in their development (emerging), EK is the only technology that offers the potential for treating the Ketchikan soil.
- EK technologies may be appropriate for all USCG SAFR soils.

Table 17 summarizes the effectiveness of the three treatment technologies for the four USCG SAFR soils.

Table 17. Summary of treatment technology effectiveness.

		Physical Separation	Chemical Extraction	Electrokinetics
Cape May		Effective	Moderately Effective	Effective
Ketchikan		Cost-prohibitive	Not tested due to soil composition	Moderately Effective
Kodiak		Ineffective	Effective	Effective
New Orleans		Moderately Effective	Moderately Effective	Presumed to be Effective

Recommendations

Based on the results of this investigation and conclusions drawn from the study, the following recommendations are provided.

- Soil remediation may be required at the four USCG sites evaluated in this study. It is recommended that initial contact with the appropriate regulatory agency be initiated to determine if clean-up actions will be required at these ranges.
- A cost analysis to identify the most cost effective treatment method for USCG soils should be conducted if clean up of the ranges is necessary.
- If clean up of the USCG SAFRs is required, EK technologies should be considered as a potential remediation technology. This technology appears to have merit for most USCG SAFRs.

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